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**THE BEHAVIOR OF  
ELECTROLYTIC SOLUTIONS  
AT ELEVATED TEMPERATURES  
AS DERIVED FROM  
CONDUCTANCE MEASUREMENTS**

**JUNE 1961**

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**BETTIS ATOMIC POWER LABORATORY, PITTSBURGH, PA.,  
OPERATED FOR THE U. S. ATOMIC ENERGY COMMISSION  
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J. M. Wright, W. T. Lindsay, Jr., and T. R. Druga

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*This project was initiated at the Bettis Atomic Power Laboratory to devise methods and techniques for measuring the conductances of reactor solutions at elevated temperatures and to interpret the results with electrolytic solution theories. This conductance information leads to a better understanding of the behavior of reactor solutions at elevated temperatures and permits reasonable speculation to be made regarding behavior of proposed reactor coolant additives.*

## THE BEHAVIOR OF ELECTROLYTIC SOLUTIONS AT ELEVATED TEMPERATURES AS DERIVED FROM CONDUCTANCE MEASUREMENTS

J. M. Wright, W. T. Lindsay, Jr., and T. R. Druga

### I. INTRODUCTION

Knowledge of the electrical conductivity of solutions is of fundamental importance in understanding the behavior of electrolytic solutions, and provides the simplest and most direct measure of the ionization of substances upon which their chemical behavior depends. In spite of its importance, only A. A. Noyes and associates (Reference 1) have successfully measured this property with reasonable precision for several substances at elevated temperatures. From their efforts, a nucleus has been made available for building general principles governing the behavior of electrolytes at elevated temperatures.

A Bettis Project was initiated to devise methods and techniques for measuring the conductances of reactor solutions at temperatures to 540F (289C) and to interpret the results with electrolytic solution theories. As a first step, the conductance data of Noyes were reviewed and interpreted, and general principles were set forth on the expected behavior of various solutions at reactor temperatures. In addition, the conductances of LiOH and

NH<sub>4</sub>OH solutions were measured at 100 to 560F. This conductance information leads to an understanding of the behavior of reactor solutions at elevated temperatures and permits reasonable speculation to be made on the behavior of proposed reactor coolant additives.

### II. REVIEW AND INTERPRETATION OF THE NOYES CONDUCTANCE DATA\*

#### A. Empirical Method for Determining Complete Ionization of Uni-univalent Electrolytes

Onsager (Reference 2) derived from theoretical considerations the following limiting equation describing the equivalent conductance of a 1-1 electrolyte:

$$\Lambda = \Lambda^{\circ} - (\alpha^* \Lambda^{\circ} + \beta^*) \sqrt{C} \quad (1)$$

\*Only 1-1 electrolytes will be discussed, since this type of electrolyte is the only kind on which sufficient data are available for application of conductance theories.



in which

$$\alpha^* = \frac{8.20411 \times 10^5}{(DT)^{3/2}}; \beta^* = \frac{82.4262}{\eta (DT)^{1/2}};$$

$\Lambda$  is the equivalent conductance at the electrolyte concentration  $C$  (equiv/liter);  $\Lambda^\circ$  is the equivalent conductance at infinite dilution;  $D$  is the dielectric constant of the solvent; and  $\eta$  is the absolute viscosity of the solvent.

Shedlovsky (Reference 3) tested the applicability of this equation over various concentration ranges by substituting measured  $\Lambda$  values in the equation, computing the  $\Lambda^\circ$  values, and noting their constancy. The equation is applicable if the computed  $\Lambda^\circ$  values remain constant with concentration and is not applicable if the computed  $\Lambda^\circ$  values deviate from constancy. It was found by using the most accurate data measured at room temperature, that the computed  $\Lambda^\circ$  values were not constant over any appreciable concentration range. However, observation was made that the computed  $\Lambda^\circ$  values (designated by  $\Lambda'_\circ$ ) plotted against the first power of the concentration, usually gave straight lines up to concentrations of about 0.1 N. On this basis, the correct  $\Lambda^\circ$  value for each electrolyte is the intercept of the  $\Lambda'_\circ$  versus  $C$  line at  $C = 0$ . Thus, Shedlovsky found empirically that completely ionized 1-1 electrolytes obey the equation

$$\Lambda'_\circ \equiv \frac{\Lambda + \beta^* \sqrt{C}}{1 - \alpha^* \sqrt{C}} = \Lambda^\circ + BC \quad (2)$$

over a concentration range of 0 to 0.1 N and temperatures of 18 and 25 C. Furthermore, it was observed that the slope,  $B$ , usually had values greater than, but within 15 percent of the Onsager limiting slope,  $(\alpha^* \Lambda^\circ + \beta^*)$ . For those salts generally considered not to be completely ionized (nitrates, chlorates, and iodates), the  $B$  values were either much less than the Onsager limiting slope or no linear relationship existed between  $\Lambda'_\circ$  and  $C$ . Thus, from conductance data, the Shedlovsky

method can be used to determine if a particular uni-univalent electrolyte is completely ionized in solution at room temperature. The method is also useful in determining the limiting conductance,  $\Lambda^\circ$ , for strong electrolytes.

To determine the kinds of curves obtained by the Shedlovsky test for different electrolytes at elevated temperature,  $\Lambda'_\circ$  versus  $C$  plots were made using the conductance data of Noyes (Reference 1) for NaCl, KCl, HCl, NaOH, AgNO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub> over the temperature range of 18 C (64.4 F) to 306 C (593 F). The first four substances, NaCl, KCl, HCl, and NaOH, are strong electrolytes at room temperature, AgNO<sub>3</sub> is slightly associated, and H<sub>3</sub>PO<sub>4</sub> is a weak electrolyte.  $\Lambda'_\circ$  versus  $C$  plots for these substances are shown in Figures 1 through 6. Appendix I presents the conductance data developed by Noyes, and Table II lists the dielectric constants and viscosities of water and the  $\alpha^*$  and  $\beta^*$  values at various temperatures. These data in Table I, along with the data of Noyes, are required to compute the  $\Lambda'_\circ$  values. Values for the dielectric constant of water from 18 to 100 C were computed by the Wyman and Ingall (Reference 4) equation,

$$D = 78.54 \left[ 1 - 4.579 \times 10^{-3}(t-25) + 1.19 \times 10^{-5}(t-25)^2 - 2.8 \times 10^{-8}(t-25)^3 \right], \quad (3)$$

and from 100 through 306C by the Akerlof and Oshry (Reference 5) equation,

$$D = \frac{5321}{T} + 233.76 - 0.9297 T + 1.417 \times 10^{-3} T^2 - 8.292 \times 10^{-7} T^3. \quad (4)$$

Values for the viscosity of water from 18 through 306 C were interpolated from smooth curves of the viscosity data given by Dorsey (Reference 6).

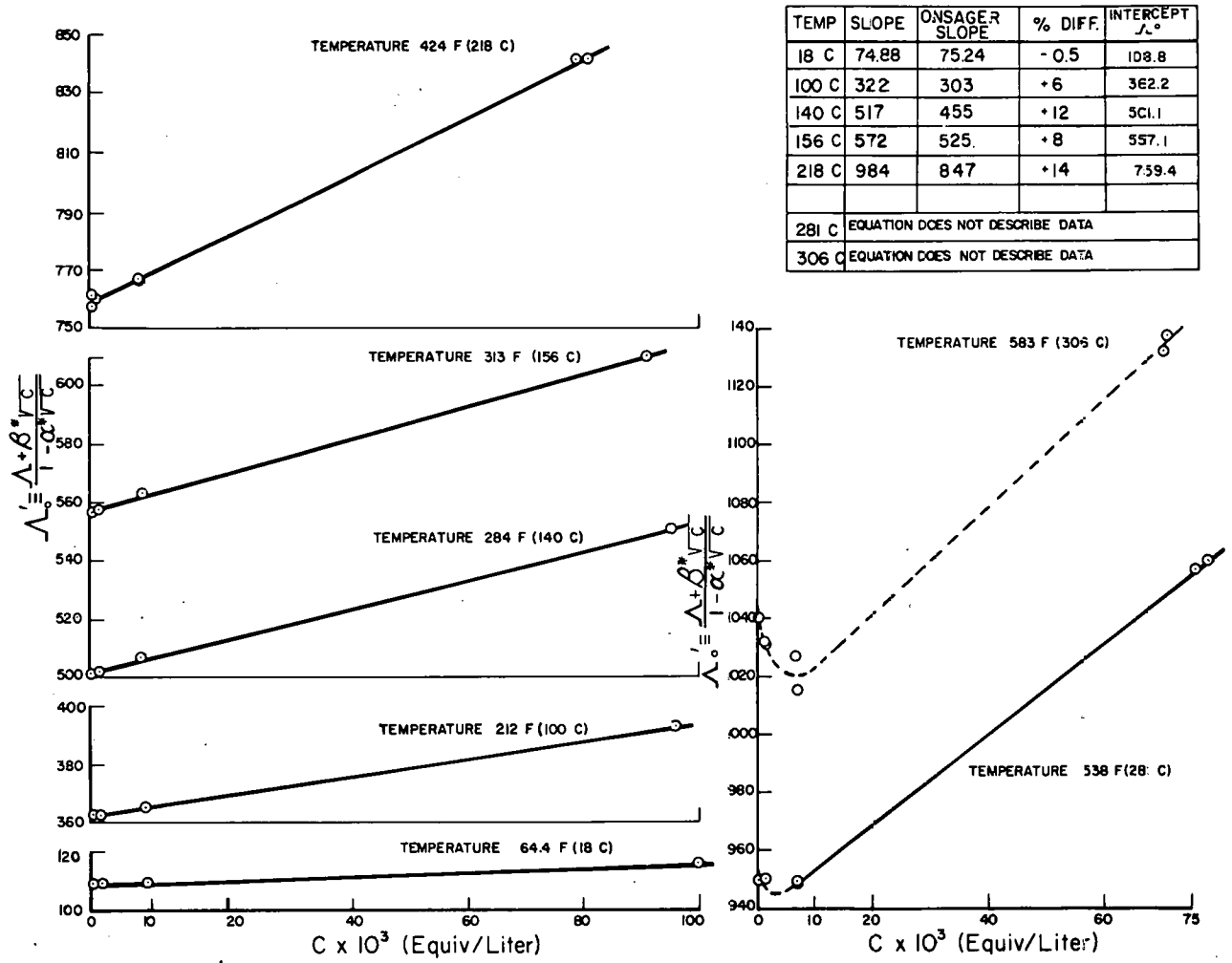


Figure 1. Shedlovsky Test on NaCl Solutions at Various Temperatures

TEMP	SLOPE	ONSAGER SLOPE	%DIFF.	INTERCEPT $\Lambda^0$
18 C	81.34	79.97	+ 2	129.8
100 C	320	314	+ 2	406.0
140 C	458	472	- 3	554.5
156 C	371	543	- 46	611.5
218 C	967	871	+ 10	817.7
281 C	1559	1336	+ 16	898.6
306 C	EQUATION DOES NOT DESCRIBE DATA			

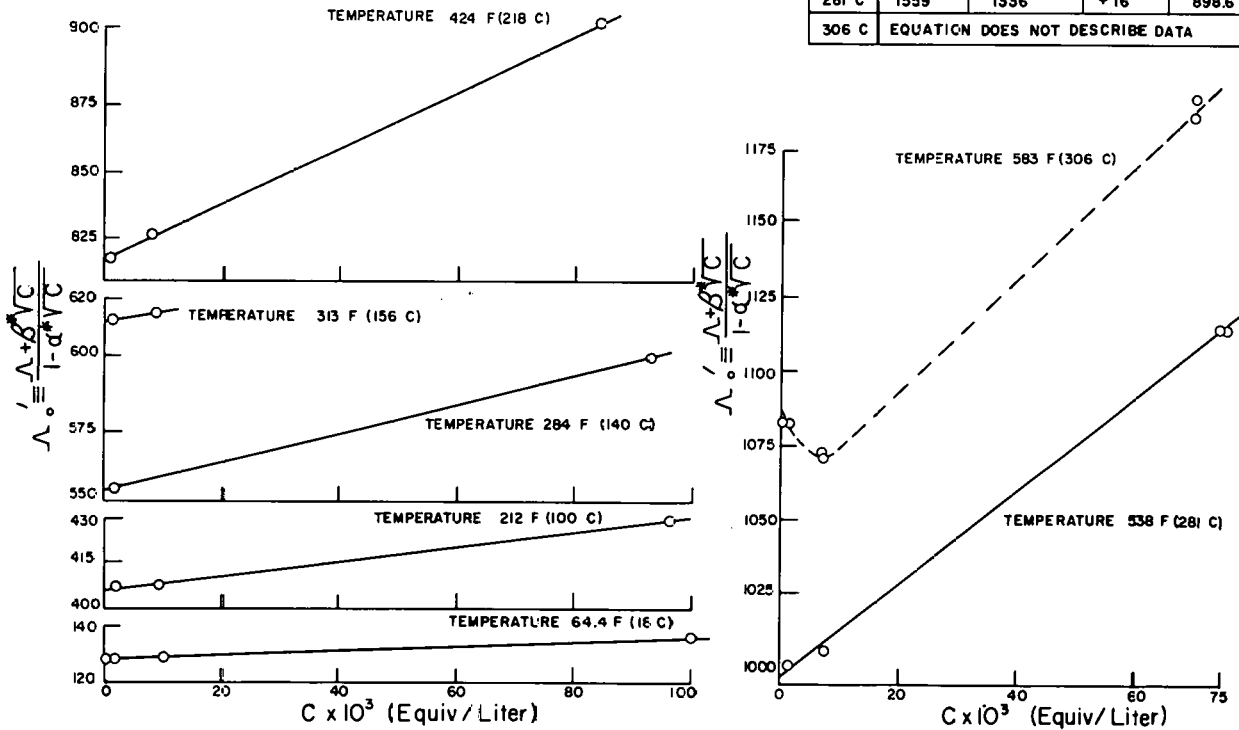
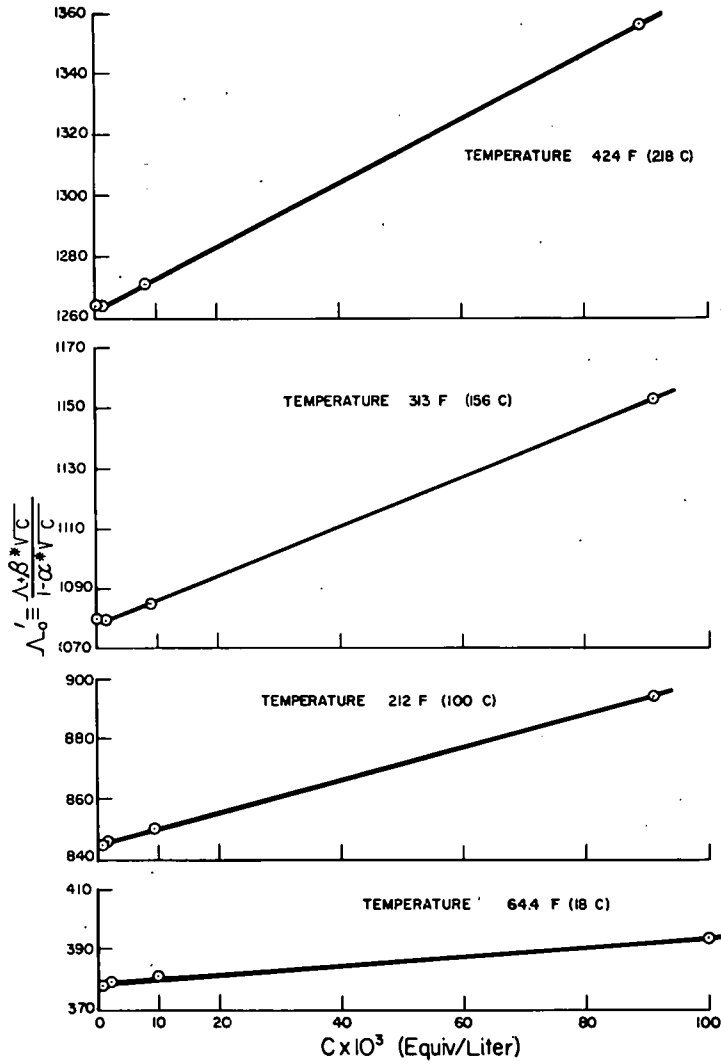


Figure 2. Shedlovsky Test on KCl Solutions at Various Temperatures



TEMP	SLOPE	ONSAGER SLOPE	% DIFF.	INTERCEPT $\Lambda_0$
18 C	157	136	+ 13	379.2
100 C	520	436	+ 16	845.4
156 C	810	698	+ 14	1078.1
218 C	1153	1061	+ 8	1263
260 C	PLOT HAS NEGATIVE SLOPE			
306 C	PLOT HAS NEGATIVE SLOPE			

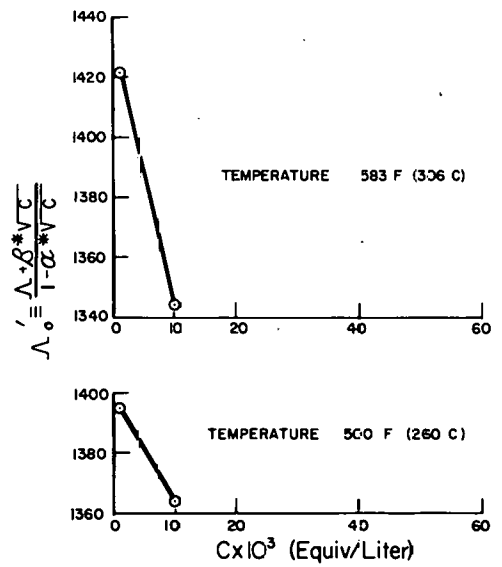


Figure 3. Shedlovsky Test on HCl Solutions at Various Temperatures

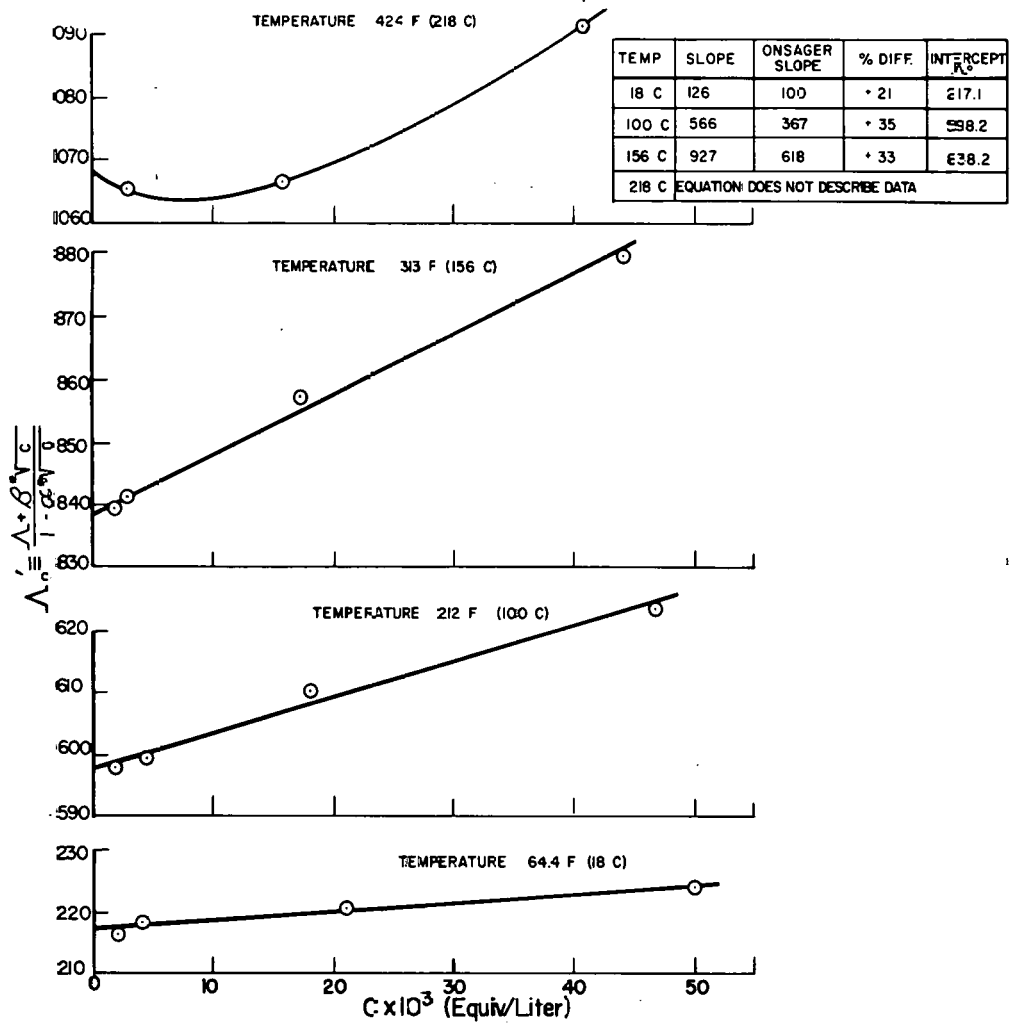


Figure 4. Shedlovsky Test on NaOH Solutions at Various Temperatures

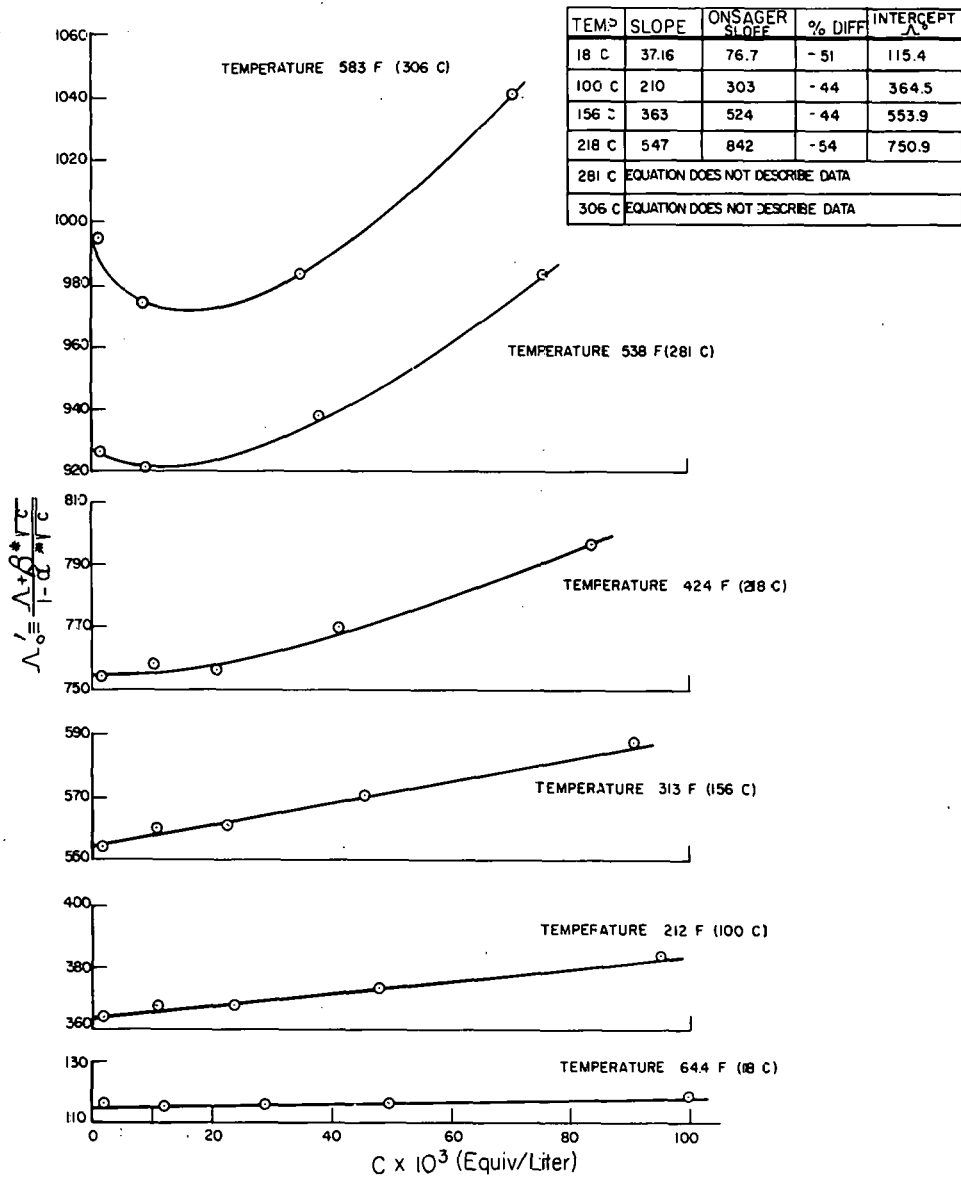


Figure 5. Shedlovsky Test on AgNO<sub>3</sub> Solutions at Various Temperatures

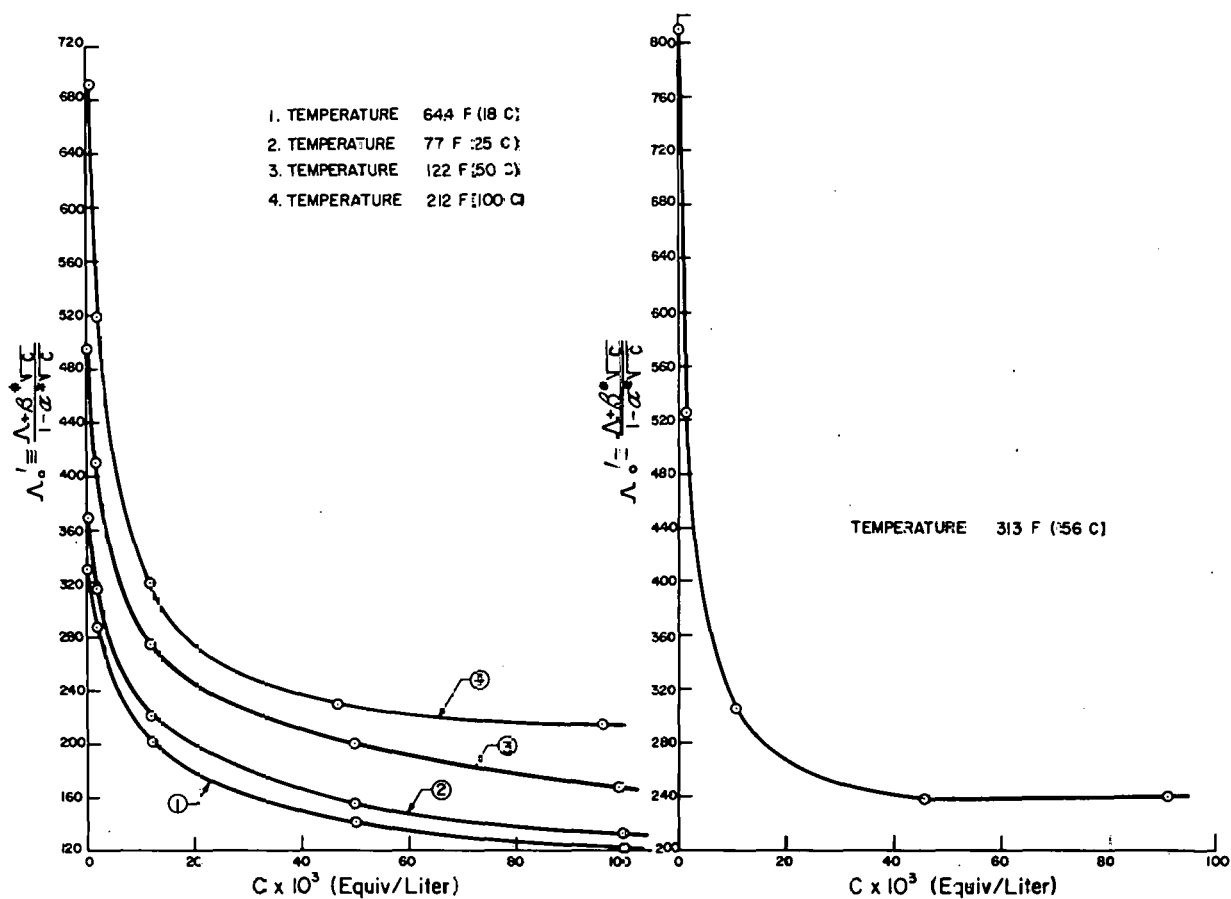


Figure 6. Shedlovsky Test on  $H_3PO_4$  Solutions at Various Temperatures

TABLE I  
PHYSICAL CONSTANTS AT VARIOUS TEMPERATURES

Temperature		Dielectric Constant	Viscosity (millipoise)	$\alpha^*$	$\beta^*$
(C)	(F)				
18	64.4	81.10	10.60	0.2261	50.60
25	77.0	78.54	8.949	0.2289	60.19
50	122	70.10	5.49	0.2406	99.75
75	157	62.62	3.81	0.2549	146.5
100	212	55.90	2.839	0.2723	201.0
128	262.4	48.57	2.215	0.3016	266.6
140	284	45.93	2.008	0.3139	298.0
156	312.8	42.61	1.793	0.3318	340.0
218	424.4	31.55	1.265	0.4254	523.5
260	500	25.19	1.093	0.5272	650.8
281	537.8	22.20	1.008	0.6013	737.3
306	582.8	18.72	0.910	0.7269	870.0

Examination of the  $\Lambda'$  versus C plots shows the Shedlovsky criterion of a linear relationship was not obeyed by  $H_3PO_4$  but it was obeyed by NaOH up to 156 C, by  $AgNO_3$ , NaCl, and HCl up to 218 C, and by KCl up to 281 C. Application of the second criterion, a B value 0 to 15 percent greater than the Onsager slope, was not obeyed by  $AgNO_3$  where the slope was between 44 and 54 percent less than the Onsager slope, or NaOH where the slope exceeded the Onsager slope by 21 to 35 percent.

Thus, if the assumption is made that the Shedlovsky criteria are applicable at any temperature, aqueous solutions of NaCl, HCl, and KCl are strong electrolytes up through temperatures of 218, 218, and 281 C, respectively. Somewhat above each of these temperatures, the electrolytes begin to associate. Using this same rule,  $H_3PO_4$  is a weak electrolyte throughout the measured temperature range. NaOH is peculiar in that the slope is greater than expected; however, NaOH is probably a strong electrolyte up to 156 C. The data on  $AgNO_3$  cannot be properly interpreted because hydrolysis occurs throughout the temperature range.

#### B. Equations Describing the Conductance Behavior of Strong 1-1 Electrolytes

Many equations have been used to describe the conductance behavior of strong 1-1 electrolytes at room temperature (Reference 7), a few of which were considered in seeking to describe the conductance behavior of electrolytes at elevated temperatures.

The Onsager limiting equation does not describe the conductance of electrolytes over any appreciable concentration range. However, the Shedlovsky linear relationship, Equation (2), has been shown to describe adequately the conductance behavior of NaCl, KCl, NaOH, and HCl to temperatures above 200 C and concentrations up to 0.1 N. Equation (2) can be rewritten as:

$$\Lambda = \Lambda^\circ - (\alpha^* \Lambda^\circ + \beta^*) \sqrt{C} + BC - \alpha^* BC^{3/2}. \quad (5)$$

In this form, it is seen to be merely an extension of the Onsager Equation (1) with the added terms,  $BC - \alpha^* BC^{3/2}$ . This equation has the disadvantage of containing the empirical parameter B.

Shedlovsky (Reference 8) proposed another empirical modification of the Onsager equation which quite accurately represents room-temperature conductances of strong electrolytes up to concentrations of about 0.01 N. This equation is:

$$\Lambda = \Lambda^\circ - \frac{\Lambda}{\Lambda^\circ} (\alpha^* \Lambda^\circ + \beta^*) \sqrt{C}, \quad (6)$$

which may be rearranged as the series,

$$\Lambda = \Lambda^\circ - (\alpha^* \Lambda^\circ + \beta^*) \sqrt{C} + \frac{(\alpha^* \Lambda^\circ + \beta^*)^2 C}{\Lambda^\circ} - \frac{(\alpha^* \Lambda^\circ + \beta^*)^3 C^{3/2}}{(\Lambda^\circ)^2} \quad (7)$$

This equation contains only one undetermined parameter and is readily applied to the calculations required later in Section II-C.

The recently developed Fuoss-Onsager equations (Reference 17) are derived entirely from theoretical grounds and contain an ion-size parameter in addition to  $\Lambda^\circ$ . It has been shown that these equations accurately represent the conductance data for strong electrolytes. However, the complex calculations required to apply the Fuoss-Onsager equations to the Noyes results have not been carried out, since a high degree of precision is required of the data to determine accurately the ion-size parameter.

To determine if Equation (6) describes the conductance behavior of electrolytes at elevated temperatures, the Noyes conductance data for NaCl, KCl, HCl, NaOH,  $AgNO_3$ , and  $H_3PO_4$  were substituted into Equation (6); the  $\Lambda^\circ$  values were computed and their constancy noted. The results of these calculations show that Equation (6) accurately represents the data for NaCl, KCl, HCl,



and NaOH to within about 0.1 percent for concentrations up to 0.01  $N$  (and to about 0.5 percent up to 0.1  $N$ ) at temperatures which show the Shedlovsky linear relationship between  $\Lambda'_e$  and  $C$ . At temperatures where the  $\Lambda'_e$  versus  $C$  plots are not linear, the computed  $\Lambda^\circ$  values are not constant, but decrease with increasing concentration. Therefore, the equation is not applicable at these temperatures.

Equation (6) describes the  $AgNO_3$  data to within about 0.1 percent up to 156 C. The equation does not describe the data for  $H_3PO_4$  at any of the measured temperatures.

Thus, if the Shedlovsky criteria for strong electrolytes is used, then Equation (6) will adequately describe the conductance behavior of these types of concentrations up to 0.01  $N$ .

### C. Determination of $\Lambda^\circ$ and the Dissociation Constant, $K$ , for Electrolytes Which Associate

The usual method (References 8 and 9) of determining  $\Lambda^\circ$  and  $K$  values for associated electrolytes is:

- 1) Define the degree of dissociation,  $\alpha$ , as:

$$\alpha = \frac{\Lambda}{\Lambda_e} \quad (8)$$

in which  $\Lambda$  is the measured equivalent conductance of the electrolyte at the concentration  $C$ , and  $\Lambda_e$  is the equivalent conductance that the electrolyte would have if only  $\alpha C$  equiv/liter of the completely dissociated electrolyte were in solution.

- 2) Substitute into Equation (8) an expression for  $\Lambda_e$  which describes the conductance behavior of a completely dissociated electrolyte. Thus,  $\Lambda$  in Equation (6) is  $\Lambda_e$  in Equation (8):

$$\Lambda = \Lambda_e = \frac{(\Lambda^\circ)^2}{\Lambda^\circ + (\alpha^* \Lambda^\circ + \beta^*) \sqrt{\alpha C}} \quad (9)$$

Substituting this expression of  $\Lambda_e$  into Equation (8) and solving for  $\alpha$  gives

$$\alpha = \frac{\Lambda}{\Lambda^\circ} \left[ \frac{z}{2} + \sqrt{1 + \left(\frac{z}{2}\right)^2} \right]^2 \equiv \frac{\Lambda}{\Lambda^\circ} s(z) \quad (10)$$

in which

$$s(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} - \dots, \quad (11)$$

and

$$z = \frac{(\alpha^* \Lambda^\circ + \beta^*) \sqrt{\alpha C}}{(\Lambda^\circ)^{3/2}} \quad (12)$$

- 3) Combine the definition of a dissociation constant,

$$K = \frac{\alpha^2 \gamma_{\pm}^2 C}{(1-\alpha)}, \quad (13)$$

with Equation (10), giving

$$\Lambda s(z) = \Lambda^\circ - \alpha^2 C \gamma_{\pm}^2 (\Lambda^\circ / K). \quad (14)$$

The mean molar activity coefficient values,  $\gamma_{\pm}$ , are calculated from the Debye-Huckel limiting law (Reference 10):

$$\log \gamma_{\pm} = \frac{-1.8242 \times 10^6 \sqrt{\alpha C}}{(T)^{3/2}} \quad (15)$$

- 4) Assume a value for  $\Lambda^\circ$  in Equation (14) and determine  $\Lambda s(z)$  and  $\alpha^2 C \gamma_{\pm}^2$  using conductance data at various concentrations. Plot the  $\Lambda s(z)$  values versus the  $\alpha^2 C \gamma_{\pm}^2$  values. If the correct  $\Lambda^\circ$  value was chosen, the intercept at  $C = 0$  is  $\Lambda^\circ$  and the slope is  $-\frac{\Lambda^\circ}{K}$ . This trial and error process is repeated until the assumed  $\Lambda^\circ$  and the  $\Lambda^\circ$  at  $C = 0$  coincide.

This procedure was used to calculate  $\Lambda^\circ$  and  $K$  values for NaCl, KCl, HCl, NaOH,  $AgNO_3$ , and  $H_3PO_4$  at those temperatures where the Shedlovsky test indicated the electrolytes were associating. Table II lists the values obtained.

TABLE II

EQUIVALENT CONDUCTANCES AT INFINITE DILUTION AND DISSOCIATION  
CONSTANTS FOR SEVERAL ELECTROLYTES AT ELEVATED TEMPERATURES

Electrolyte	Temperature (C)	$\Lambda^\circ$	K
NaCl	281	952	0.22
	306	1042	0.093
KCl	281	1000	0.49
	306	1086	0.12
HCl	260	1409	0.12
	306	1470	0.035
NaOH	218	1068	0.55
AgNO <sub>3</sub>	218	754	0.92
	281	931	0.15
H <sub>3</sub> PO <sub>4</sub>	3-6	1007	0.069
	18	341	8.19 x 10 <sup>-3</sup>
	25	379	7.63 x 10 <sup>-3</sup>
	50	513	5.53 x 10 <sup>-3</sup>
	75	634	3.92 x 10 <sup>-3</sup>
	100	741	2.69 x 10 <sup>-3</sup>
	125	846	1.74 x 10 <sup>-3</sup>
	156	934	1.10 x 10 <sup>-3</sup>

D. Use of the Bjerrum Theory to Determine if Ion-Pair Formation Explains the Decrease in Ionization of Electrolytes at Elevated Temperatures

Table II shows the ionization of all electrolytes decreases with increasing temperature. To determine if this decrease could be caused by ion-pair formation, recourse was had to the Bjerrum (Reference 11). While this theory has recently been superseded by more elegant variations which do not require certain of the arbitrary assumptions which are necessary in the Bjerrum treatment (Reference 17), it has been used extensively in the past and is still used to explain the low-conductance behavior of strong electrolytes in media of low-dielectric constant (such as water-alcohol mixtures). In such media, the conductance of a strong electrolyte decreases as the dielectric constant of the solvent decreases. Since the dielectric constant for water decreases as temperature increases, the decrease in ionization constant for the electrolytes shown in Table II could be produced by ion-pair formation as opposed to covalent bond formation. Bjerrum assumed an electrolytic solution composed of rigid, nonpolarizable spherical ions in

a medium of a fixed macroscopic dielectric constant. With this model, Bjerrum calculated the probability of finding two oppositely charged ions a distance,  $r$ , from each other and noted that the probability possessed a minimum at a distance,  $q$ . Then it was assumed that ion-pair formation took place if two oppositely charged ions were closer to each other than the distance  $q$  and that ion-pair formation did not take place if the ions were farther from each other than the distance  $q$ . Bjerrum derived relationships between the constant for dissociation of an ion-pair,  $K$ , the dielectric constant of the medium  $D$  and the temperature of the solution  $T$  and the mean distance approach  $a$ , between the centers of the two ions forming the pair.

These relationships are:

$$1/K = \frac{4\pi N}{1000} \left( \frac{|z_+ z_-| \epsilon^2}{DkT} \right)^3 Q(b), \quad (16)$$

$$Q(b) = \int_2^b e^Y Y^{-4} dY, \quad (17)$$

and

$$b = \frac{|z_+ z_-| \epsilon^2}{a D k T} \quad (18)$$

These equations were applied to the K values shown in Table II to determine how the calculated mean distance of approach,  $a$ , varied with temperature and dielectric constant. Values for K and DT were substituted into Equation (16) and Q(b) determined. The value of b was determined from a plot of Q(B) versus b. The mean distance of approach,  $a$ , was determined using Equation (18). Table III shows the variation of  $a$  with temperature. Also included in this table are the distances,  $q$ , at which the probability function possesses a minimum and ionic radii values obtained from X-ray diffraction data.

According to the Bjerrum theory, ion-pair formation takes place when the mean distance of closest approach for the ions lies between the  $q$  values and the sum of the ionic radii. This condition is satisfied by NaCl, KCl, NaOH, and perhaps HCl at the higher temperatures. Therefore, these electrolytes are considered to show ion-pair formation. However, the Bjerrum theory is not applicable to AgNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> solutions since their  $a$  values are less than the sum of the ionic radii (except for AgNO<sub>3</sub> at 218 C). This indicates a force is

operative which is different than the coulomb attractive force used in the Bjerrum derivation. Presumably, H<sub>3</sub>PO<sub>3</sub> does not form ion-pairs but associates by covalent-bond formation. Extensive hydrolysis must also be considered to effect the behavior of AgNO<sub>3</sub> solutions.

### III. MEASUREMENT OF THE CONDUCTANCES OF LiOH AND NH<sub>4</sub>OH SOLUTIONS OVER THE TEMPERATURE RANGE OF 100 TO 520 F.

#### A. Description of the Apparatus

Figure 7 shows the arrangement of the apparatus. The solution was pumped from the 50-liter, polyethylene bottle source tank successively through a mixed-bed, ion-exchange resin\*; a low-temperature, high-pressure conductivity cell; a

\*The mixed bed resin was of the same form as the solution which was passed through it. For the water runs, as-received H-OH form mixed-bed resin was used. For the LiOH or NH<sub>4</sub>OH runs, the H-OH form resin was converted to the Li<sup>+</sup> OH<sup>-</sup> or NH<sub>4</sub><sup>+</sup> + OH<sup>-</sup> form by passing strong solutions of these bases through the resin column. Each column was washed with 30 to 40 liters of demineralized water before being used in order to remove any soluble amines which might be present.

TABLE III  
CHANGE IN  $a$  VALUES;  $q$  VALUES AND THE DIELECTRIC CONSTANT OF WATER WITH TEMPERATURE

Electrolyte	Temperature (C)	Dielectric Constant	$q = \frac{ Z_+ Z_-  \epsilon^2}{2 DRT}$		Sum of Ionic Radii (Å) <sup>(13)</sup>
			(Å <sup>o</sup> )	a(Å)	
NaCl	281	22.2	6.79	5.11	2.76
	306	18.72	7.71	4.60	
KCl	281	22.20	6.79	6.11	3.14
	306	18.72	7.71	5.17	
HCl	260	25.19	6.22	3.01	not known
	306	18.72	7.71	2.57	
NaOH	218	31.55	5.39	5.26	2.35 (Na O <sup>=</sup> )
AgNO <sub>3</sub>	218	31.55	5.39	4.07	4.00 from
	281	22.20	6.79	3.88	(Ag N <sup>5</sup> (N-O) O <sup>=</sup> )
	306	18.72	7.71	2.22	
H <sub>3</sub> PO <sub>4</sub>	18	81.10	3.54	0.25	3.30 from (P (P-O) O <sup>=</sup> )
	25	78.54	3.57	0.25	
	50	70.10	3.69	0.25	
	75	62.62	3.83	0.25	
	100	55.93	4.01	0.24	
	128	48.57	4.29	0.24	
	156	42.61	4.57	0.24	

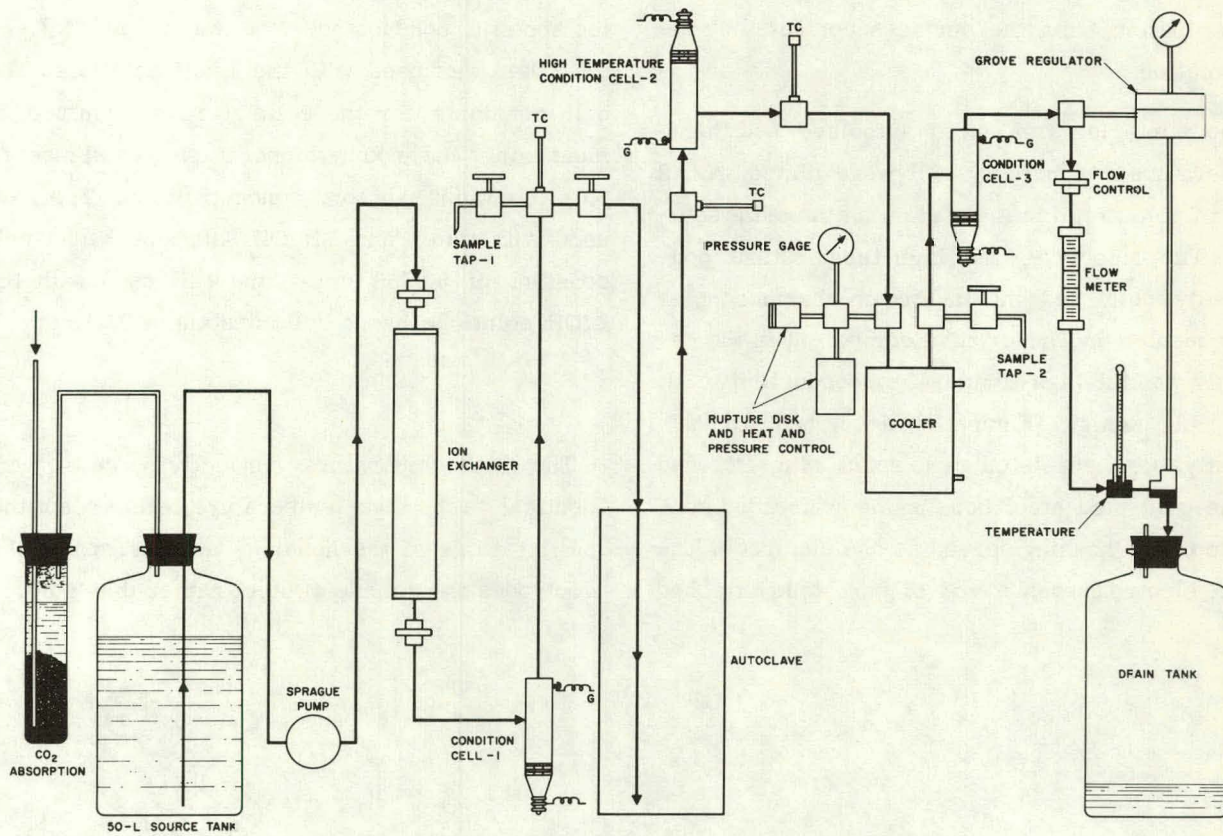


Figure 7. Schematic Arrangement of Apparatus



heated, gold-plated autoclave; a high-temperature, high-pressure conductivity cell; a cooler; a low-temperature, high-pressure conductivity cell; a flow regulator valve; a flow meter; and finally to drain. A regulator set the system pressure at 2000 psi. The entire assembly was made as compact as practical to lessen heat losses and to minimize contamination from the surfaces contacted by the hot solution.

The interior of the autoclave and high-temperature conductivity cell were plated with 2 mils of gold to minimize contamination of the solution. The autoclave, the high-temperature conductivity cell, and the in-stream thermocouples were insulated. The critical component in the assembly was the high-temperature conductivity cell. The cell design (Figure 8) developed for this investigation, consisted of a spark plug attached to the gold-clad steel housing by a threaded connection. The housing served as one electrode. The other electrode was a rod of pure gold attached

to a steel rod which extended from the bottom of the spark plug through the top of the plug and allowed electrical contact with the solution in the cell. The two electrodes were insulated from each other by the alumina part of the plug. Two different high-temperature cells were used in this work; one cell was used in the determinations of the specific conductances of water and  $\text{NH}_4\text{OH}$ , the other was used with the  $\text{LiOH}$  solutions. The cell constants for the cells were determined by measuring the room-temperature resistance of  $\text{KCl}$  solutions at five concentrations. The cell used with water and  $\text{NH}_4\text{OH}$  solutions had a cell constant of  $0.0566 \text{ cm}^{-1}$ ; the cell used with the  $\text{LiOH}$  solutions had a cell constant of  $0.219 \text{ cm}^{-1}$ .

The low-temperature conductivity cells were identical to the high-temperature cells except that the interiors of the housings and the spark plug electrodes were made of steel rather than gold.

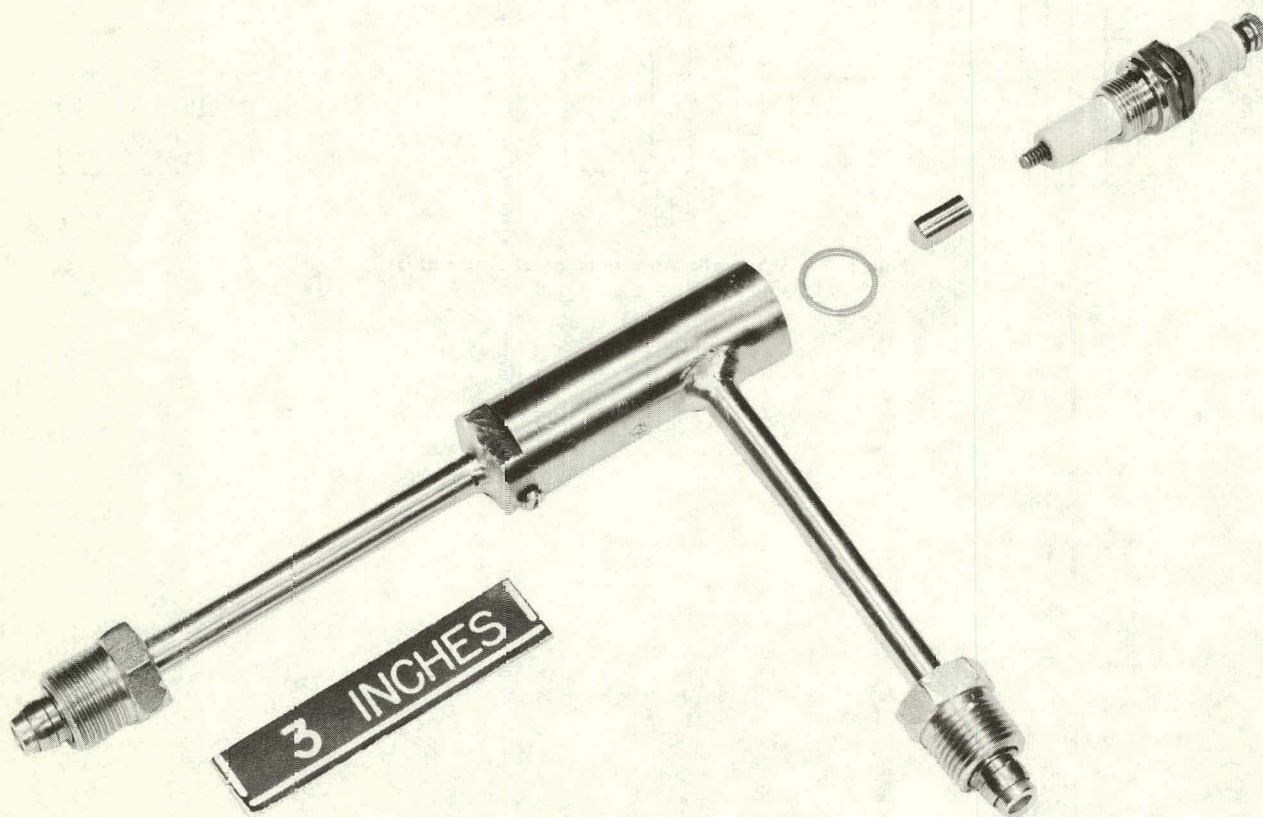


Figure 8. Component Parts of High-Temperature, High-Pressure Conductivity Cell

The leads from the conductivity cell electrodes were connected to a Type No. 650A Impedance Bridge manufactured by the General Radio Co. This instrument is accurate to 1.0 percent and operates at a frequency of 1000 cps. A Dumont cathode-ray oscilloscope was used as the detector.

#### B. Operational Procedure

Fifty liters of distilled water were placed in the source tank and nitrogen gas was bubbled through the water for about 30 minutes to remove  $\text{CO}_2$  and  $\text{O}_2$ . A known quantity of the electrolyte solution was poured into the source tank and nitrogen gas was bubbled through the solution for about 30 minutes to assure complete mixing. The top of the source tank was capped and two polyethylene tubing leads were inserted through the cap. One lead was connected to the pump; the other lead was connected to a  $\text{CO}_2$  absorption bottle, which was partially filled with a LiOH solution.

While the solution was being mixed, the autoclave was drained, isolated by the flow control valve and the valve immediately before the autoclave, and evacuated. The valve before the autoclave was opened and the solution was allowed to fill the system. The flow control valve was set at 50 cc/min. When the solution was shown to be of constant composition throughout the system (as indicated by the conductivity measurements on the three cells), the autoclave heaters were turned on and the temperature of the solution, measured at the autoclave outlet, was raised to 580 F. When this temperature was reached, the autoclave heaters were turned off and the solution flow rate was increased from 50 to 200 cc/min. This increase in rate essentially eliminated any temperature drop across the high-temperature conductivity cell. Conductance and temperature readings were made simultaneously every 3 to 10 F as the temperature decreased from 580 F to about 100 F. The runs

were usually terminated at this point. Low-temperature conductance readings were taken to determine if contamination of the solutions occurred in the heated portion of the system.

During a run, samples of the solution were taken at the taps upstream of the autoclave and downstream of the cooler. Each sample was analyzed for the most conductive specie in the solution.

#### C. The Specific Conductance of the Water

Specific conductance measurements of the water used in preparing solutions were made over the temperature range of 100 to 570 F several times during the course of this work. These measurements served as a check on the cleanliness of the apparatus and are subtracted from the total measured conductivity of the solution in calculating the specific conductance of the electrolyte. It should be pointed out that these measurements do not yield the correct conductance values of pure water at the elevated temperatures since: (1) the initial water contained some impurities, and (2) pickup of additional impurities occurred in the system.

The conductivity data obtained in each of the water runs are shown in Figure 9. The first three runs were made prior to the  $\text{NH}_4\text{OH}$  determinations. The fourth run was made between the  $\text{NH}_4\text{OH}$  and LiOH determinations. The conductivity of the cooled water leaving the system is also shown.

#### D. Equivalent Conductances of $\text{NH}_4\text{OH}$ Solutions over the Temperature Range of 100 to 560 F

The resistances of the  $\text{NH}_4\text{OH}$  solutions were measured over the room-temperature concentration range of 0.00473 to 0.0933 N and a temperature range of 100 to 560 F. The equivalent conductances of the solutions were calculated using the standard definition of an equivalent conductance.

Figure 10 shows a plot of the data from each determination. The room-temperature concentrations of the  $\text{NH}_4\text{OH}$  solutions were obtained by

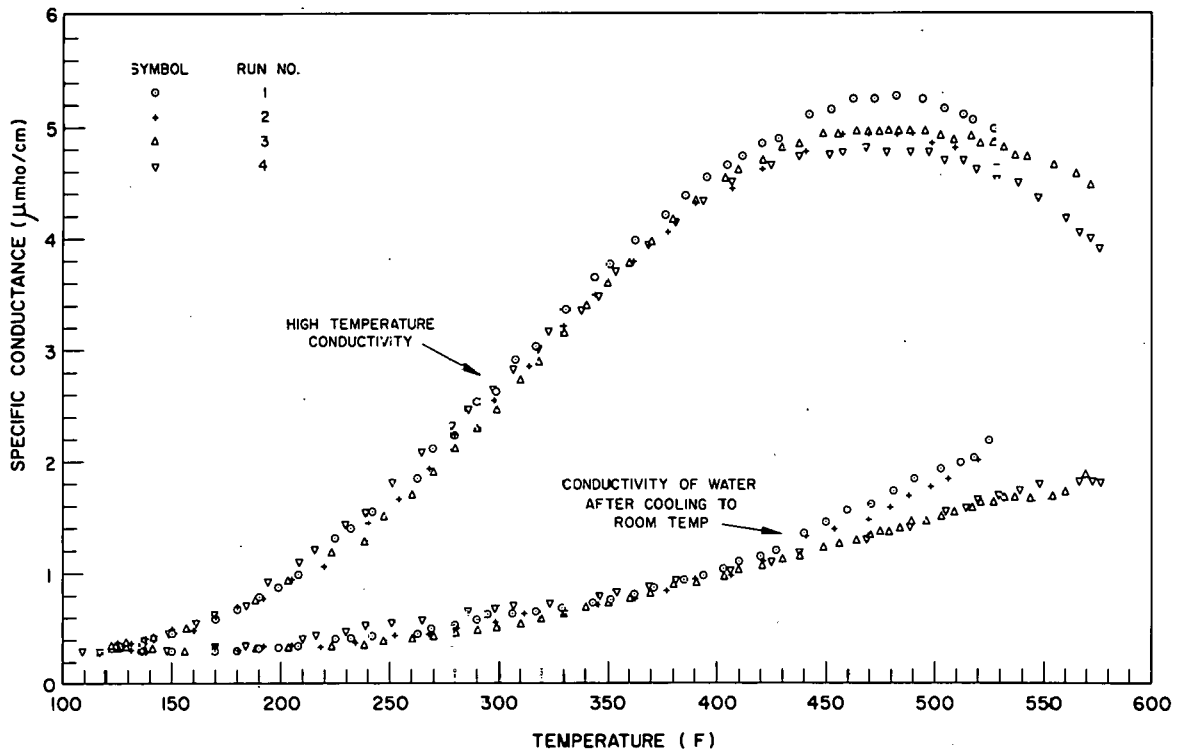


Figure 9. Specific Conductance of Water Used in the Experiments

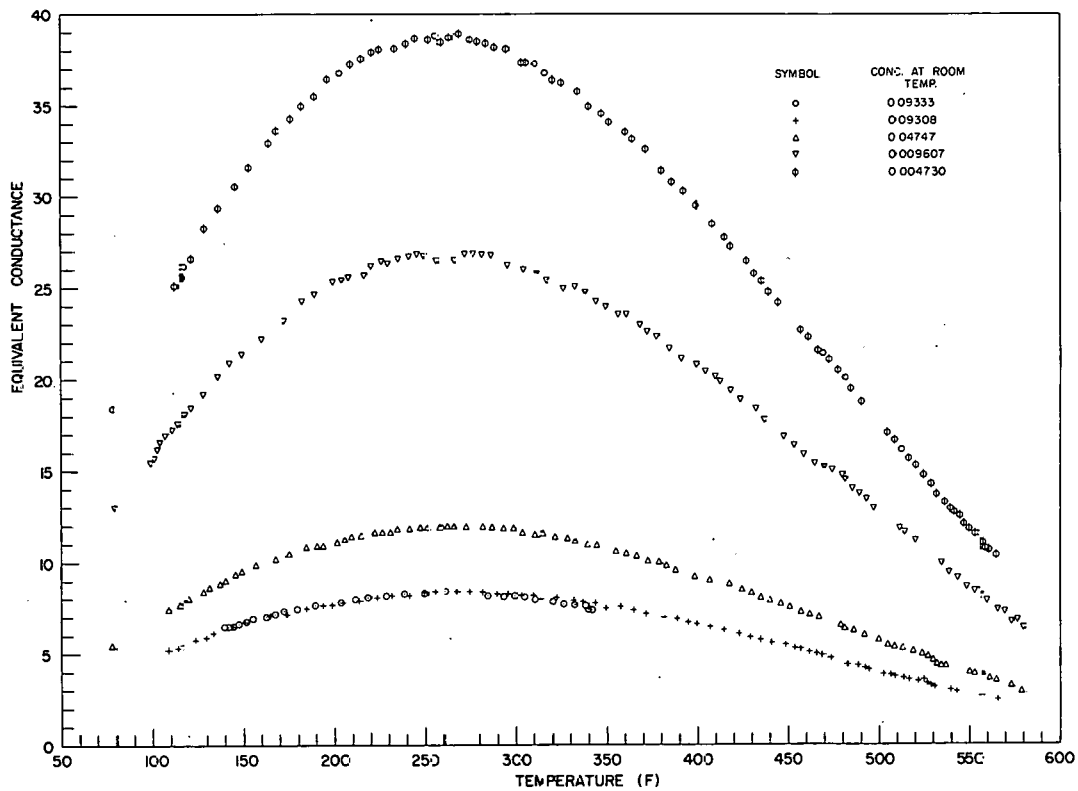


Figure 10. Variation of the Equivalent Conductances of  $\text{NH}_4\text{OH}$  Solutions with Temperature

titration against standardized 0.1 N  $\text{H}_2\text{SO}_4$  or standardized 0.01 N HCl using methyl red as the indicator. The  $\text{NH}_4\text{OH}$  concentrations remained essentially constant throughout all determinations. Baker and Adamson CP grade ammonium hydroxide was used in preparing the initial solutions.

#### E. Equivalent Conductances of LiOH Solutions Over the Temperature Range of 100 to 520 F

The resistances of LiOH solutions were measured over the room-temperature concentration range of 0.00073 N to 0.0015 N and a solution temperature range of 100 to 520 F. Since LiOH is a strong electrolyte, it was necessary to use very dilute solutions to maintain the conductance within reasonable limits.

The use of very dilute solutions introduced two difficulties: (1) Initially, titration of the solution to determine  $\text{OH}^-$  concentration yielded erratic results. It was determined that the solutions were being contaminated by  $\text{CO}_2$  from the air during sampling and analysis. To prevent contamination, plastic hoods were placed around the sample taps and titration vessels to permit  $\text{N}_2$  blanketing of the samples at all times. Thereafter, titration results were reproducible to better than 1 percent. (2) The  $\text{OH}^-$  concentration was not constant during a run. The changes were followed as a function of solution temperature by titrating samples taken periodically from the system. Plots were made of the room-temperature concentrations as a function of solution temperature and the concentrations for any temperature were estimated by interpolation. It was difficult to decide whether the inlet concentration, the outlet concentrations, or an average of these should be used to calculate the equivalent conductances. The impurity (or impurities) which entered the solutions and tended to neutralize the  $\text{OH}^-$  could have come from the thermal decomposition of nonionized, slightly soluble materials in the ion-exchange resins; or from surfaces of the heated autoclave, the high-temperature conductivity cell,

or the steel tubing located between the high-temperature conductivity cell and the cooler. The interference by impurities was not appreciably decreased by increasing the flow rate of solution through the system. This indicated the concentration change occurred in the autoclave, which could not be adequately flushed because of its large volume. If this is true, the resistance readings of the high-temperature cell were affected by the change. Therefore, the outlet concentration was chosen as the true concentration of the solution. The conductance data are shown in Figure 11.

#### F. Best Values for the Equivalent Conductances of $\text{NH}_4\text{OH}$ and LiOH At Temperature Intervals of 40 F

The best values of the equivalent conductances for the  $\text{NH}_4\text{OH}$  solutions and the LiOH solutions at various concentrations and at temperature intervals of 40 F were obtained from smooth plots of the data shown in Figures 10 and 11. The values obtained are shown in Tables IV and V.

#### G. The Behavior of LiOH Solutions at Elevated Temperatures

Darken and Meier (Reference 13) measured the equivalent conductances of LiOH, NaOH, and KOH solutions at 25 C as a function of concentration and compared their ionization characteristics using the Shedlovsky test described in Section II-A. They found the  $\Lambda'_o$  versus C plot for LiOH had a slight dip in it and concluded that LiOH behaves as a weak electrolyte. An ionization constant of 1.2 was calculated. NaOH showed very nearly complete ionization and the KOH showed complete ionization.

The Shedlovsky test was applied to the Bettis LiOH data using the equivalent conductance values shown in Table V. The  $\Lambda'_o$  versus C plots are shown in Figure 12. These plots show that the slopes of the lines became more negative as the temperature of the solution increased, indicating LiOH becomes less ionized as the solution temperature is increased.



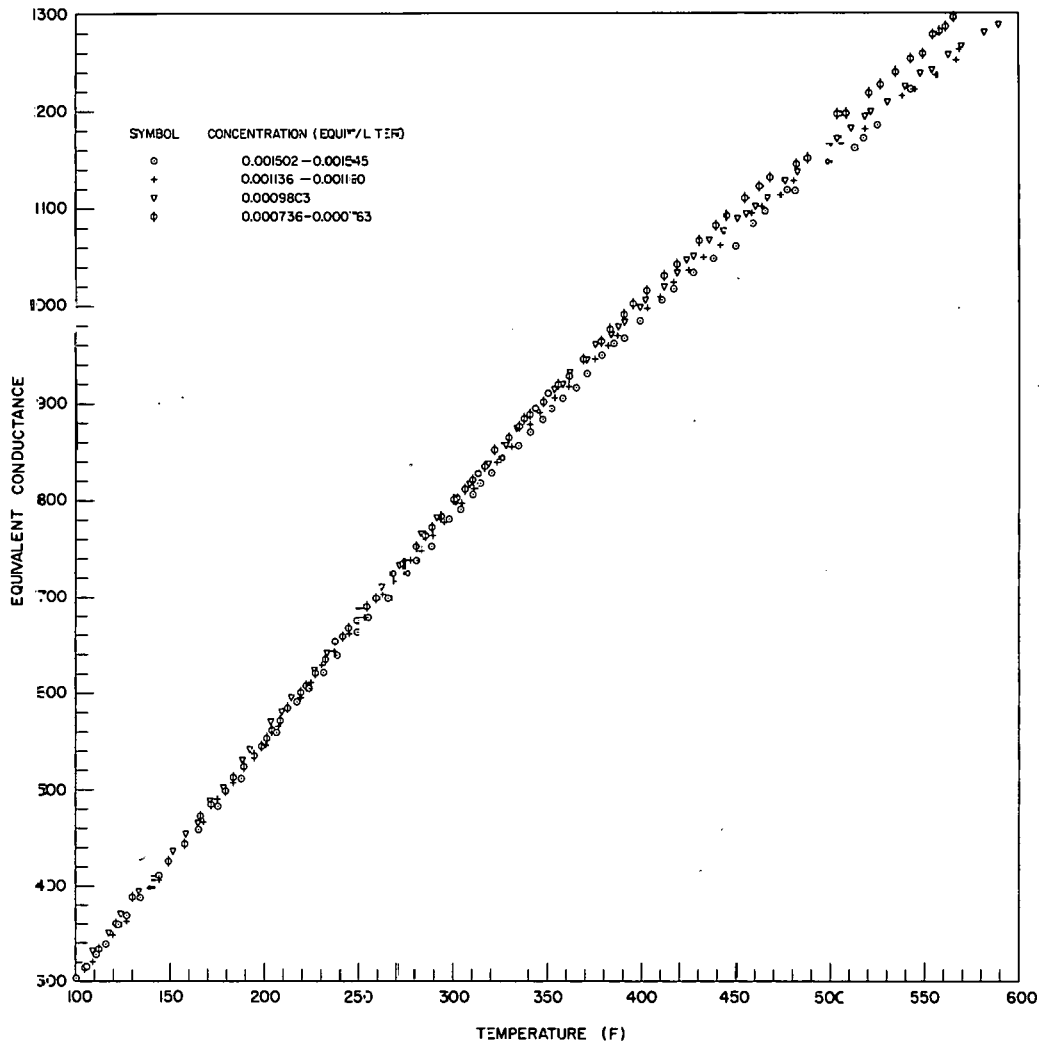


Figure 11. Variation of Equivalent Conductances of LiOH Solutions with Temperature

TABLE IV  
BEST VALUES FOR THE EQUIVALENT CONDUCTANCES OF NH<sub>4</sub>OH SOLUTIONS AT VARIOUS TEMPERATURES AND CONCENTRATIONS

Temperature (F)	Run 1		Run 2		Run 3		Run 4		Run 5	
	Equivalent Conductance (mho-cm <sup>2</sup> /eq)	Conc. at Temperature (eq/liter)	Equivalent Conductance (mho-cm <sup>2</sup> /eq)	Conc. at Temperature (eq/liter)	Equivalent Conductance (mho-cm <sup>2</sup> /eq)	Conc. at Temperature (eq/liter)	Equivalent Conductance (mho-cm <sup>2</sup> /eq)	Conc. at Temperature (eq/liter)	Equivalent Conductance (mho-cm <sup>2</sup> /eq)	Conc. at Temperature (eq/liter)
80	4.13	0.09333	-	-	-	-	13.2	0.009604	-	-
120	5.83	0.09203	5.70	0.09179	8.16	0.04682	18.3	0.009471	26.4	0.004665
160	7.04	0.09122	7.01	0.09099	10.0	0.04641	22.2	0.009388	32.5	0.004624
200	7.93	0.08990	7.80	0.08967	11.2	0.04574	25.2	0.009252	36.6	0.004557
240	8.31	0.08820	8.31	0.08798	12.00	0.04488	26.8	0.009078	38.5	0.004471
280	8.39	0.08649	8.48	0.08627	12.00	0.04400	26.9	0.008901	38.5	0.004384
320	7.97	0.08461	8.16	0.08439	11.6	0.04305	25.4	0.008707	36.6	0.004288
360			7.56	0.08230	10.5	0.04198	23.5	0.008492	33.7	0.004182
400			6.73	0.07997	9.4	0.04079	20.8	0.008251	29.5	0.004064
440			5.75	0.07750	8.0	0.03953	17.7	0.007997	24.8	0.003938
480			4.68	0.07548	6.6	0.03804	14.6	0.007696	20.2	0.003790
520			3.59	0.07122	5.17	0.03633	11.2	0.007348	15.4	0.003619
560			2.64	0.06711	3.74	0.03423	7.95	0.006924	10.9	0.003410

TABLE V

BEST VALUES FOR THE EQUIVALENT CONDUCTANCES OF LiOH SOLUTIONS AT VARIOUS TEMPERATURES AND CONCENTRATIONS

Temperature (F)	Run 1		Run 2		Run 3		Run 4	
	Equivalent Conductance (mho-cm <sup>2</sup> /eq)	Conc. at Temperature (eq/liter)	Equivalent Conductance (mho-cm <sup>2</sup> /eq)	Conc. at Temperature (eq/liter)	Equivalent Conductance (mho/cm <sup>2</sup> /eq)	Conc. at Temperature (eq/liter)	Equivalent Conductance (mho/cm <sup>2</sup> /eq)	Conc. at Temperature (eq/liter)
120	350	0.001524	347	0.001143	359	0.0009668	352	0.0007525
160	448	0.001510	448	0.001131	459	0.0009583	453	0.0007458
200	546	0.001488	548	0.001113	559	0.0009444	552	0.0007351
240	644	0.001460	650	0.001089	660	0.0009266	655	0.0007198
280	737	0.001432	744	0.001066	757	0.0009085	754	0.0007025
320	828	0.001398	833	0.001041	844	0.000888	844	0.0006845
360	911	0.001360	919	0.001014	929	0.0008668	930	0.0006649
400	990	0.001317	996	0.0009832	1002	0.0008422	1012	0.0006435
440	1057	0.001272	1064	0.0009512	1076	0.0008162	1087	0.0006211
480	1122	0.001220	1130	0.0009138	1137	0.0007855	1157	0.0005954
520	1178	0.001159	1190	0.0008711	1200	0.0007500	1220	0.0005660

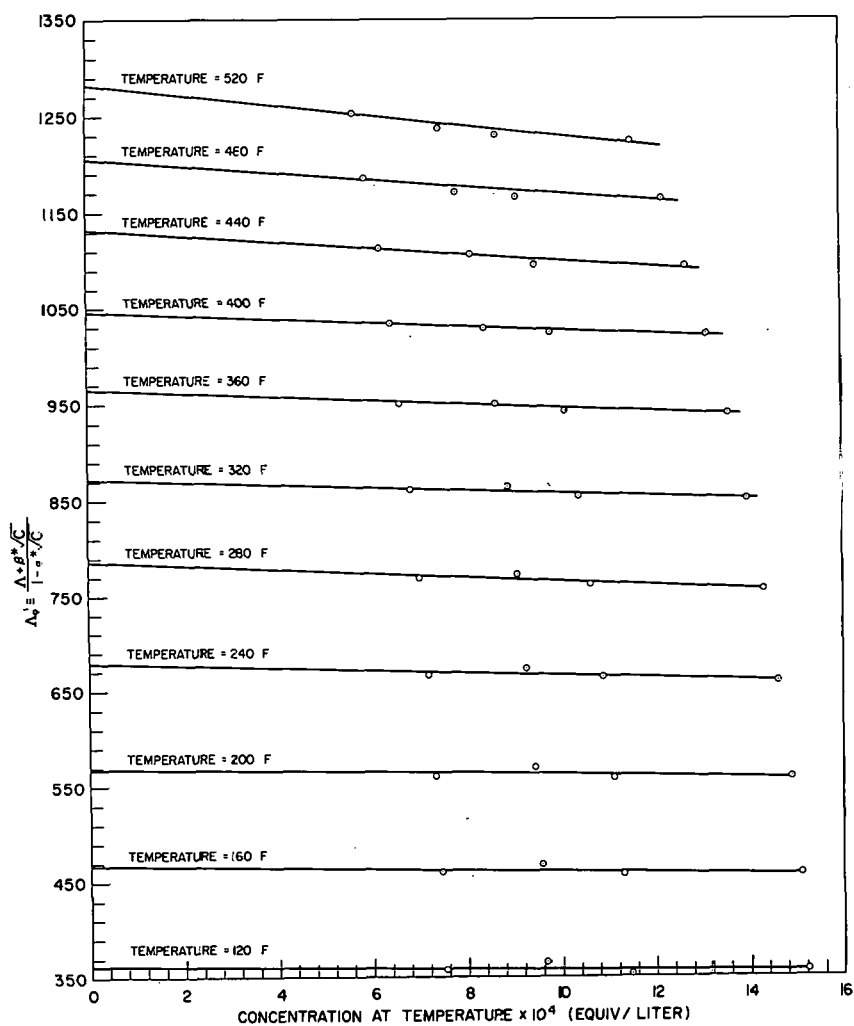


Figure 12. Shedlovsky Test for the Ionization of LiOH Solutions

The equivalent conductances at infinite dilution and the ionization constants were computed using the method outlined in Section II-C. The final results are shown in Table VI. The  $\Lambda_{\infty} S(Z)$  versus  $\alpha^2 C \gamma_{\pm}^2$  plots and the change in the ionization constants with temperature are shown in Figures 13 and 14, respectively.

It is clear from the  $K$  versus temperature plot (Figure 14) that the number of  $\text{Li}^+$  and  $\text{OH}^-$  ions in solution decreases as the temperature of the solution increases. The theory of Bjerrum presented in Section II-D was used to determine whether

TABLE VI  
EQUIVALENT CONDUCTANCES AT INFINITE DILUTION AND THE IONIZATION CONSTANTS FOR LiOH AT TEMPERATURES FROM 120 F to 520 F

Temperature (F)	$\Lambda^{\circ}$ (mho-cm <sup>2</sup> /eq)	(K molar scale)
120	360.7	0.128
160	466.7	0.0685
200	569.1	0.0742
240	679.1	0.0456
280	786.1	0.0310
320	873.9	0.0435
360	965.1	0.0396
400	1046	0.0414
440	1133	0.0255
480	1206	0.0234
520	1283	0.0172

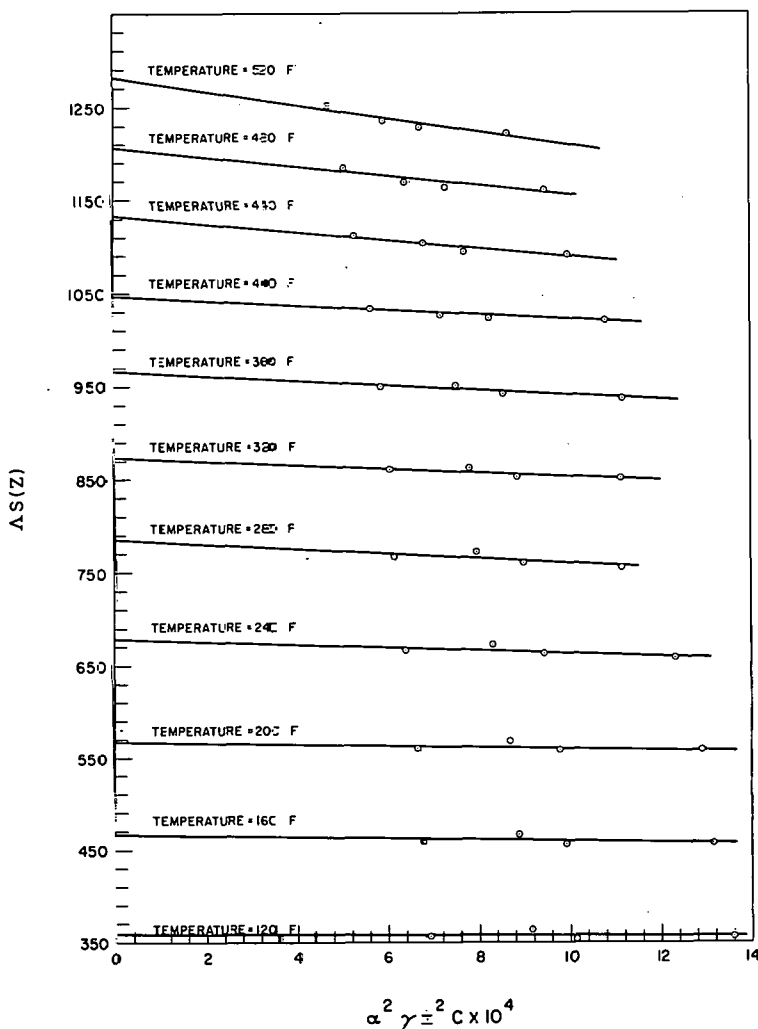


Figure 13. Determination of  $\Delta^0$  and  $K$  by  $\Delta S(Z)$  Versus  $\alpha^2 \gamma_{\pm}^2 C \times 10^4$  Plot

this decrease could be caused by ion-pair formation. The  $a$  values and the distances,  $q$ , at which the probability function possesses a minimum are shown in Table VII. This table shows the calculated  $a$  values are less than the sum of the ionic radii, indicating that some force in addition to simple ion-ion attraction is probably operative between the  $\text{Li}^+$  and  $\text{OH}^-$  ions.

Johnston (Reference 15) showed from the Noyes conductance data that a log-log plot of the equivalent conductances at infinite dilution for salts versus viscosities of water at various temperatures yielded straight lines, and further noted that bases and acids did not follow this relationship. Figure 15 illustrates this plot. The Bett's LiOH data follows

this relationship as shown in Figure 16. The equation relating the  $\Lambda^0$  for LiOH and the viscosity of water is:

$$\Lambda^0 = 7.4 \eta_0^{-0.75} \quad (20)$$

#### H. Behavior of $\text{NH}_4\text{OH}$ Solutions at Elevated Temperatures

The conductances of  $\text{NH}_4\text{OH}$  solutions were measured by A. A. Noyes (Reference 1) at 212, 313, 424, and 583 F. The method consisted of: (1) placing an ammonium hydroxide solution of known concentration in a platinum lined autoclave and measuring the room temperature (18 C) conductance of the solution; (2) heating the solution to some predetermined temperature and measuring the conductance, and (3) cooling the solution to room temperature and remeasuring the conductance. The best

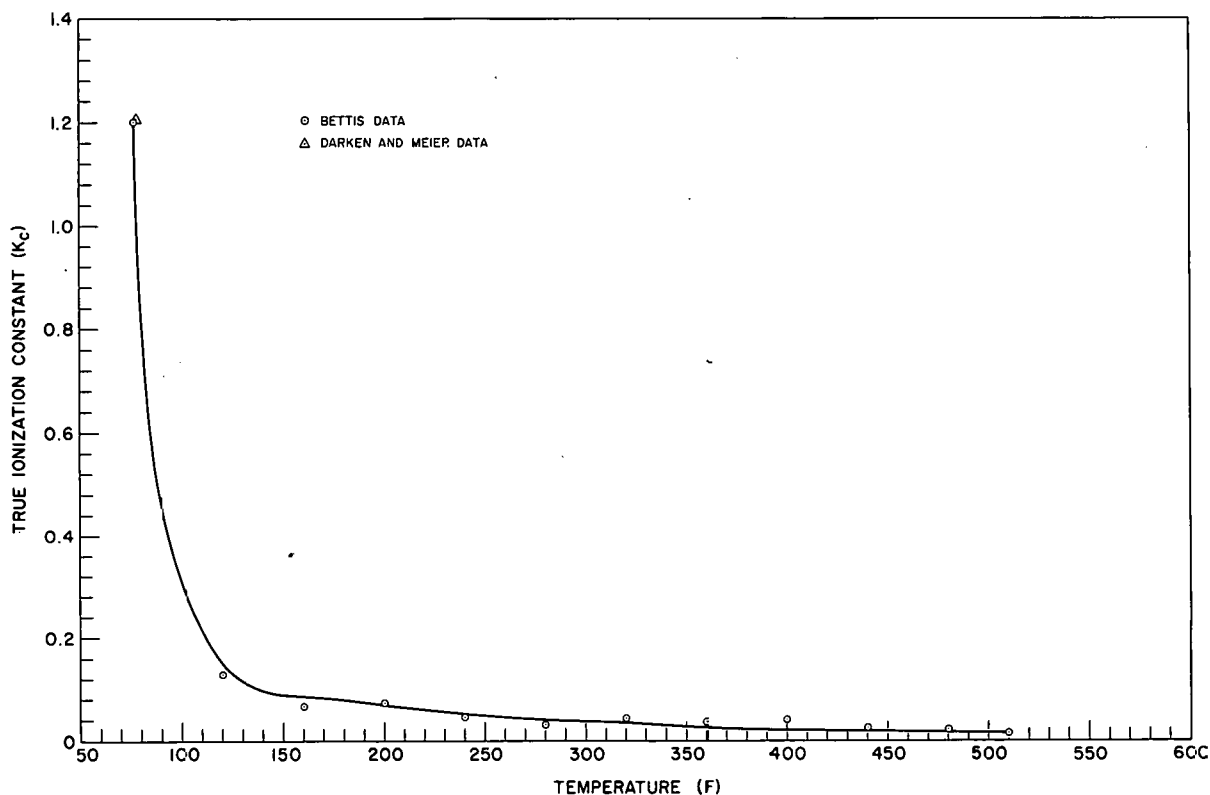


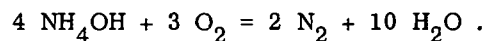
Figure 14. Variation of Ionization Constant of LiOH with Temperature

TABLE VII  
CALCULATED MEAN DISTANCES OF CLOSEST APPROACH FOR LiOH

Temperature (F)	Dielectric Constant	$q = \frac{1Z+Z-1\epsilon^2}{2DKT}$	$a$ (A°)	Sum of Ionic Radar (Li <sup>+</sup> + O <sup>=</sup> ) A°
77	78.5	-	-	2.41
120	70.1	3.65	1.28	
160	63.3	3.78	0.77	
200	57.1	3.94	0.84	
240	51.5	4.12	0.81	
280	46.4	4.32	0.80	
320	41.8	4.55	0.95	
360	37.6	4.81	1.02	
400	33.8	5.11	1.16	
440	30.2	5.47	1.16	
480	26.8	5.89	1.27	
520	23.6	6.42	1.37	

value data of Noyes are compared against the Bettis best value data in Table VIII. The percentage difference between the two sets of data was seen to increase with increasing temperature. This indicated impurities were leaching into the Bettis solutions or decomposition was taking place in the Noyes solutions. Noyes observed that the final

room-temperature conductances of his solutions were less than the initial conductances and attributed this change to a catalytic oxidation of NH<sub>4</sub>OH by the platinum lining of the autoclave:



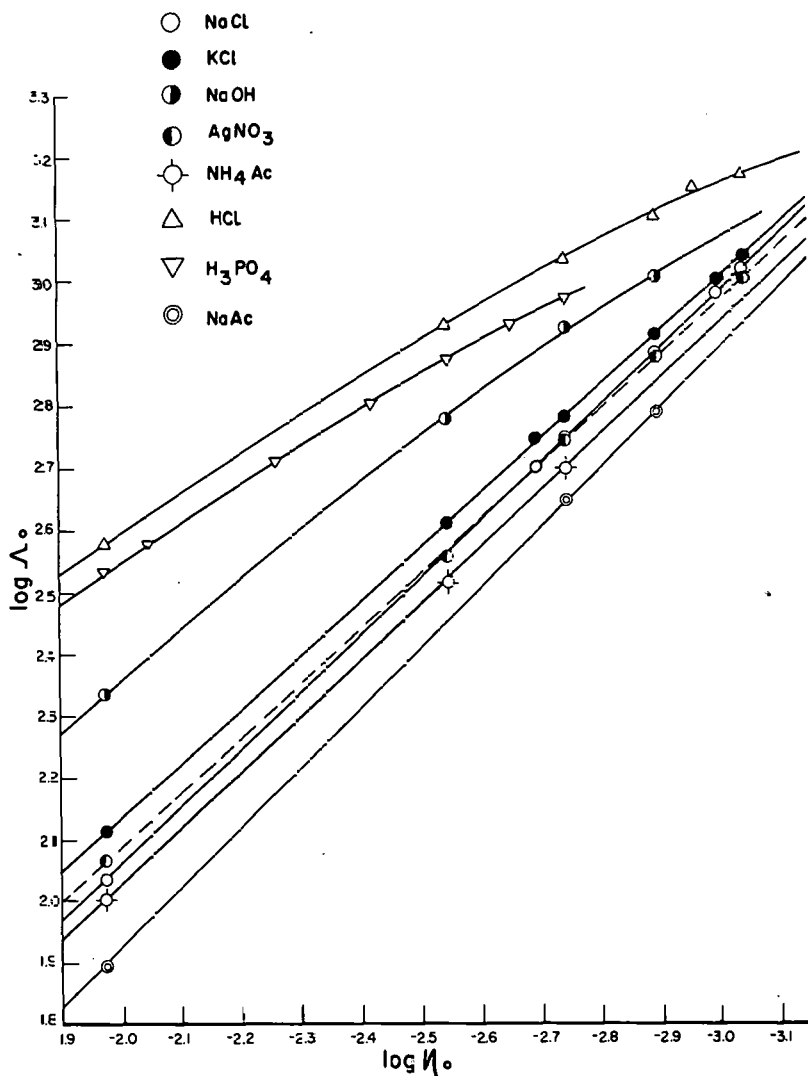


Figure 15.  $\log \Lambda_0$  Versus  $\log \eta_0$  for Several Electrolytes

TABLE VIII  
BEST VALUES FOR THE EQUIVALENT CONDUCTANCES OF  $\text{NH}_4\text{Cl}$  SOLUTIONS  
OBTAINED BY A. A. NOYES AND BETTIS

Temperature (F)	Concentration at Temperature (equiv/liter)	Equivalent Conductance		% Difference (Bettis-Noyes)
		Bettis Data	Noyes Data	
212	0.0100	24.6	23.5	4.5
	0.0400	12.1	11.8	2.5
	0.0900	8.03	7.84	2.4
313	0.0100	24.1	21.7	10.0
	0.0400	12.0	11.2	6.7
	0.0900	7.94	7.55	4.9
424	0.0100	17.2	15.4	10.5
	0.0400	8.58	7.63	11.1
	0.0900	5.71	5.08	11.0

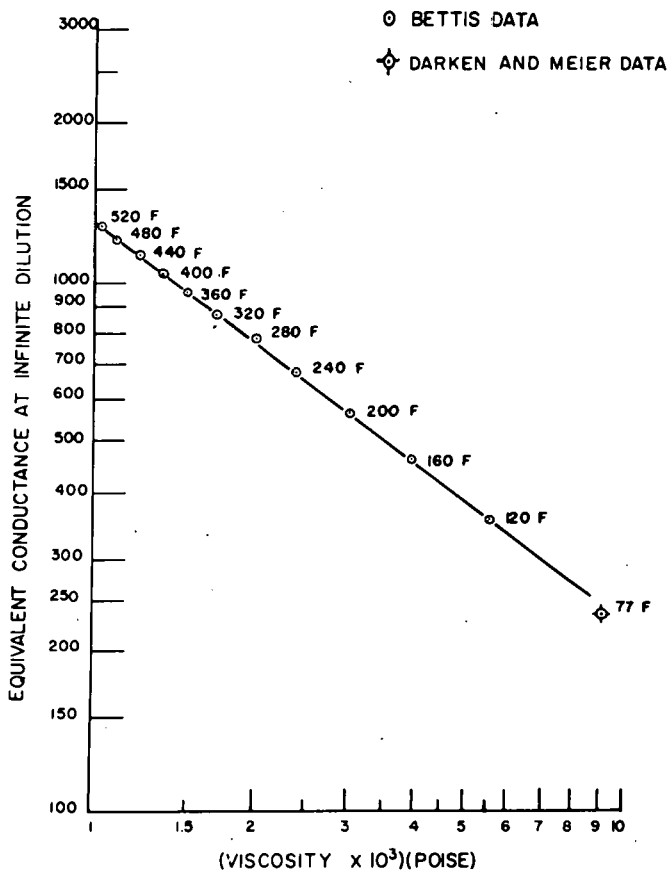


Figure 16. Variation of the Equivalent Conductances of LiOH at Infinite Dilution with the Viscosity of the Solvent

The conductance decrease amounted to about 1 percent for the solutions heated to 212 F and to about 2 percent for the solutions heated to 424 F. The Bettis analyses showed no apparent change in  $\text{NH}_4\text{OH}$  concentration on passage through the gold-lined system.

The  $\Lambda^\circ$  and K values for  $\text{NH}_4\text{OH}$  cannot be determined by the method described for LiOH since the equivalent conductance values for  $\text{NH}_4\text{OH}$  are about two orders of magnitude less than the limiting conductances,  $\Lambda^\circ$ , and extrapolation of the data to  $C = 0$  is very inaccurate. The  $\Lambda^\circ$  values were determined using the Noyes  $\Lambda^\circ$  values for NaOH,  $\text{NH}_4\text{Ac}$ , and NaAc at various temperatures and the Kohlrausch limiting conductance law. The dissociation constants were determined by substituting the  $\text{NH}_4\text{OH}$  best value data (Table IV) into Equations (8) and (9) and solving for  $\alpha$ ; then, solving for  $\gamma_{\pm}$  using Equation (15) and substituting the  $\alpha$  and

$\gamma_{\pm}$  values into Equation (13). The final  $\Lambda^\circ$  and K values at various temperatures are shown in Table IX.

#### IV. THE ION-PRODUCT OF WATER AT ELEVATED TEMPERATURES

Heretofore, all reactor coolant data have been related to the room-temperature pH of reactor coolants. One of the main purposes of this report is to determine the true pH of reactor coolants at reactor temperatures. The ion-product of water must be known before these values can be determined.

Noyes, Kato, and Sosman (Reference 13) have determined the ion-product of water at elevated temperatures by a series of experiments which consisted of: (1) measuring the conductances of solutions containing a hydrolyzable salt at different initial salt concentrations, and (2) measuring the conductances of solutions of the hydrolyzable salt mixed with added amounts of one of the hydrolysis products. The addition of the hydrolysis product represses the hydrolysis of the salt, and the conductance measured is essentially that conductance which the salt would have if it did not hydrolyze. The difference in conductances found in steps (1) and (2) is a measure of the hydrolysis of the salt.

TABLE IX  
 $\Lambda^\circ$  AND K VALUES FOR  $\text{NH}_4\text{OH}$   
AT VARIOUS TEMPERATURES

Temperature, (F)	$\Lambda^\circ$	K (molar units)
120	387	$2.08 \times 10^{-5}$
160	507	$1.79 \times 10^{-5}$
200	618	$1.49 \times 10^{-5}$
240	727	$1.13 \times 10^{-5}$
280	827	$9.05 \times 10^{-6}$
320	927	$6.41 \times 10^{-6}$
360	1023	$4.39 \times 10^{-6}$
400	1110	$2.92 \times 10^{-6}$
440	1192	$1.75 \times 10^{-6}$
480	1262	$9.38 \times 10^{-7}$
520	1326	$6.16 \times 10^{-7}$
560	1380	$2.40 \times 10^{-7}$



The ion-product of water is calculated using the hydrolysis constant of the salt and the ionization constants of the hydrolysis products. Table X lists the Noyes  $K_w$  values for water at five different temperatures. These  $K_w$  values in Table X may not be accurate since a close examination of the data shows that in some cases insufficient amounts of the hydrolysis products were added for complete suppression of the salt hydrolysis. Several different approaches were taken in an attempt to recalculate the ion products from the data; however, none of the methods appeared to be improvements over the empirical method of Noyes and until more experimental data are available to obtain a more accurate expression to represent changes in conductance of mixtures, the values for the ion-product for water, listed in Table X, will have to be used.

#### V. CHANGE IN THE pH OF $H_2O$ , $LiOH$ , AND $NH_4OH$ SOLUTIONS WITH TEMPERATURE

The pH of pure water at various temperatures was calculated using the equation,

$$pH = -\log (H^+) = -\log K_w^{1/2}, \quad (21)$$

in which  $(H^+)$  represents the molar hydrogen ion concentration. The  $K_w$  values at various temperatures are shown in Table X.

The procedure used to calculate the pH of  $LiOH$  and  $NH_4OH$  solutions at various temperatures was:

- 1) Assume an ammonium hydroxide or lithium hydroxide solution to have a certain pH at room temperature.

TABLE X

#### THE ION-PRODUCT OF WATER AT VARIOUS TEMPERATURES

Temperature (C)	Temperature (F)	Ion-Product of Water $K_w$
18	64.4	$0.64 \times 10^{-14}$
100	212	$4.8 \times 10^{-13}$
156	313	$2.23 \times 10^{-12}$
218	424	$4.61 \times 10^{-12}$
306	583	$1.68 \times 10^{-12}$

- 2) From the assumed pH and the equation

$$pH = -\log (H^+) \quad (22)$$

calculate the  $(H^+)$  concentration.

- 3) From the relationships

$$K_w = (H^+) (OH^-) \quad (23)$$

$$K_{Base} = \frac{(M^+) (OH^-)}{(MOH)} \quad (24)$$

$$(OH^-) = (M^+) + (H^+) \quad (25)$$

$$(M^+) = \alpha C \quad (26)$$

$$(MOH) = C(1 - \alpha) \quad (27)$$

in which the molar concentration of the base is  $C$  and  $\alpha$  is the degree of ionization of the base, it can be shown that:

$$\alpha = \frac{K_{Base}}{K_{Base} + \frac{K_w}{(H^+)}} \quad (28)$$

and

$$C = \frac{K_w - (H^+)^2}{\alpha (H^+)} \quad (29)$$

Substitute the room-temperature values for  $K_{Base}$ ,  $K_w$ , and  $(H^+)$  into Equation (28) and solve for  $\alpha$ . Substitute  $\alpha$  into Equation (29) and solve for  $C$ .

- 4) Determine the concentration of the solution at various temperatures by dividing the specific volume of the solution at the various temperatures into the room temperature concentration,  $C$ .

- 5) From the relationships listed in step (3), it can be shown that

$$K_{Base} (H^+)^3 + (K_w + K_{Base} \cdot C) (H^+)^2 - K_w \cdot K_{Base} (H^+) = K_w^2 \quad (30)$$

Use the values for  $K_{Base}$ ,  $C$ , and  $K_w$  at the temperature in question, and calculate  $(H^+)$ .

6) Substitute ( $H^+$ ) into Equation (22) and calculate the pH of the solution.

Table XI and Figure 17 show the pH values of neutral water at various temperatures, the pH values for  $NH_4OH$  solutions having a room temperature pH of 8.0 and 9.5, and the pH values of LiOH solutions having room temperature pH values of 9.0 and 10.5.

It is clear from this table that, for the  $NH_4OH$  concentrations specified for reactor coolants, the coolant at reactor temperatures is more basic than neutral water (pH = 5.75) by only 0.5 pH unit, whereas, a reactor coolant containing LiOH is 1.5 to 2 pH units more basic than neutral water. Differences in concentrations of insoluble corrosion products found in the two coolants may well be attributed to this difference in basicity of the solutions. Suspensoids are very sensitive to changes in environment and additions of electrolytes can easily cause flocculation or agglomeration and settling. The corrosion mechanism may also be directly affected by the pH of the solution. The added basicity in LiOH coolants may be the direct cause for the lower levels of suspended corrosion products observed in plants using this coolant as opposed to plants using coolant containing  $NH_4OH$ .

## VI. SUMMARY AND CONCLUSIONS

A. Criteria applied to room-temperature conductances for determining complete ionization of 1-1 electrolytes were applied to the A. A. Noyes high-temperature conductance data obtained

on NaCl, HCl, KCl, NaOH,  $AgNO_3$ , and  $H_3PO_4$  solutions. It was found that the first four electrolytes behave as strong electrolytes up through temperatures of 218, 218, 281, and 156 C, respectively. Application of the Bjerrum theory showed that, somewhat above each of these temperatures, these electrolytes begin to associate by ion-pair formation.  $H_3PO_4$  solutions associate at room temperature and above.  $AgNO_3$  solutions appear to associate at all temperatures, but no conclusions can be drawn because of complications caused by hydrolysis. The equivalent conductances at infinite dilution and the dissociation constants for each of the aforementioned electrolytes were calculated over their measured temperature ranges by the Shedlovsky method. The dissociation constants decrease with increasing temperature.

B. An apparatus was constructed and measurements were made on the conductances of LiOH and  $NH_4OH$  solutions over the temperature range of 100 F (38 C) to 520 F (271 C). The equivalent conductances at infinite dilution and the dissociation constants were calculated for these solutions by the Shedlovsky method. Application of the Bjerrum theory indicated LiOH that some attractive force, in addition to ion-ion attraction, was acting between the  $Li^+$  and  $OH^-$  ions.

C. The pH of reactor coolants using LiOH or  $NH_4OH$  was calculated from the dissociation constants for water, LiOH, and  $NH_4OH$  at elevated temperatures. Reactor coolants containing  $NH_4OH$  are only 0.5 of a pH unit more basic than water at reactor temperature whereas a reactor coolant containing LiOH is 1.5 to 2 pH units more basic

TABLE XI  
CHANGE IN THE pH OF WATER,  $NH_4OH$ , AND LiOH SOLUTIONS AS A  
FUNCTION OF TEMPERATURE

Temperature (F)	Water	pH		pH	
		$NH_4OH$ Solutions		LiOH Solutions	
77	7.00	8.00	9.50	9.00	10.50
212	6.16	6.41	7.77	7.30	8.80
313	5.83	5.96	6.96	6.62	8.12
424	5.67	5.71	6.41	6.29	7.76
583	5.89	5.90	6.28	6.64	8.12

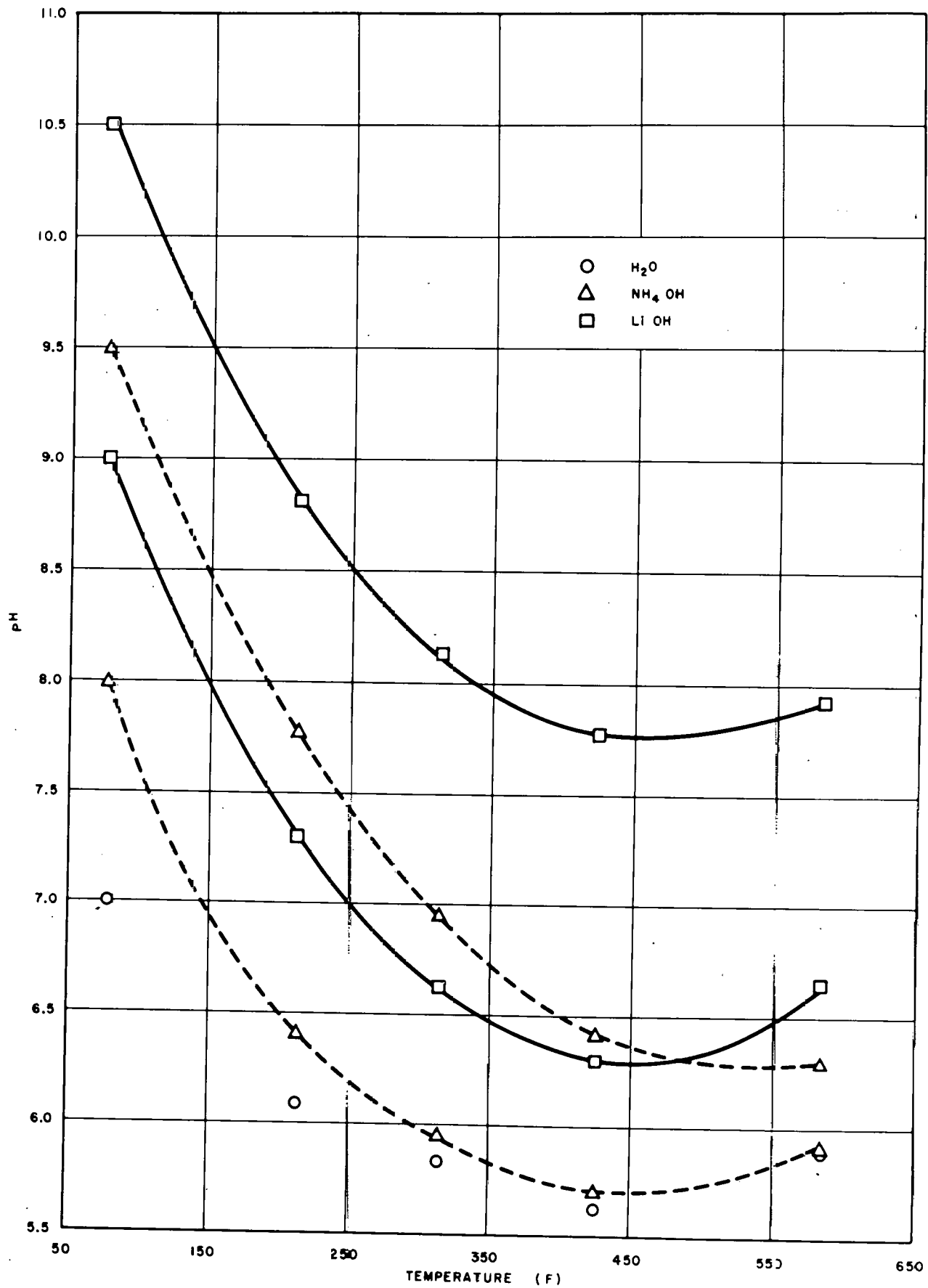


Figure 17. Variations of pH of Water, LiOH, and NH<sub>4</sub>OH Solutions with Temperature

than water. The differences in concentrations of suspended corrosion products found in the different reactor coolants may well be explained by this difference in basicity.

APPENDIX I. DATA COMPILED BY NOYES ON VARIOUS ELECTROLYTES AT ELEVATED TEMPERATURES (TABLE I-1)

TABLE I-1

DATA COMPILED BY NOYES ON VARIOUS ELECTROLYTES AT ELEVATED TEMPERATURES

Temperature (C)	$\Omega$	C x 10 <sup>3</sup> (equiv/liter)
<u>A. NaCl</u>		
18	107.36	0.500
18	105.54	2.000
18	101.96	10.000
18	92.01	100.000
100	355.8	0.479
100	349.4	1.917
100	349.3	1.924
100	336.0	9.590
100	296.8	95.900
140	491.5	0.463
140	482.0	1.850
140	462.5	9.260
140	405.0	95.200
156	546.0	0.456
156	535.0	1.820
156	513.0	9.110
156	445.5	91.100
218	745	0.420
218	740	0.422
218	727	1.680
218	725	1.690
218	689.5	8.43
218	690.0	8.44
218	586.0	84.40
218	585.0	86.60
281	925	0.373
281	900	1.480
281	836	7.470
281	834	7.530
281	678	75.700
281	676	77.600

TABLE I-1

DATA COMPILED BY NOYES ON VARIOUS ELECTROLYTES AT ELEVATED TEMPERATURES (Cont)

Temperature (C)	$\Omega$	C x 10 <sup>3</sup> (equiv/liter)
306	1011	0.346
306	973	1.330
306	972	1.330
306	895	6.930
306	883	6.990
306	691	70.200
306	694	70.500
<u>B. KCl</u>		
18	128.11	0.500
18	126.35	2.000
18	122.43	10.000
18	112.03	100.000
100	393.3	1.920
100	377.7	9.580
100	536.7	95.900
140	535	1.850
140	449	93.000
156	589	1.824
156	563	9.100
218	782.0	1.680
218	746.0	8.440
218	635.5	84.400
281	949	1.490
281	889	7.510
281	730	74.300
281	726	75.600
306	1051	0.347
306	1022	1.380
306	937	6.960
306	935	6.990
306	730	70.200
306	735	70.500
<u>C. HCl</u>		
18	375.2	0.500
18	373.6	1.998
18	368.1	9.990
18	350.6	99.900
100	836	0.479
100	827	1.998
100	808	9.590
100	756	95.900
156	1065	0.456
156	1049	1.820
156	1018	9.110
156	934	91.100

TABLE I-1

DATA COMPILED BY NOYES ON VARIOUS  
ELECTROLYTES AT ELEVATED  
TEMPERATURES (Cont)

Temperature (C)	$\Lambda$	$C \times 10^3$ (equiv/liter)
218	1243	0.422
218	1220	1.690
218	1174	8.430
218	1040	84.300
260	1332	2.000
260	1226	10.000
306	1337	2.000
306	1162	10.000

## D. NaOH

18	212.1	2.038
18	211.8	4.033
18	205.5	21.520
18	200.6	50.240
100	582.1	1.947
100	576.9	3.851
100	560.6	18.360
100	542.7	47.050
156	812.6	1.850
156	803.3	3.678
156	774.1	17.440
156	745.3	44.710
218	1008.8	3.404
218	941.7	16.140
218	891.6	41.380

E. AgNO<sub>3</sub>

18	112.2	1.998
18	107.2	12.480
18	104.0	24.950
18	100.2	49.860
18	94.6	99.800
100	351.0	1.916
100	335.0	11.970
100	321.5	23.950
100	308.0	47.830
100	289.0	95.800
156	532	1.821
156	504	11.370
156	481	22.750
156	457	45.430
156	426	91.200
218	720	1.685
218	672	10.520
218	635	21.070
218	597	42.130
218	548	84.600

TABLE I-1

DATA COMPILED BY NOYES ON VARIOUS  
ELECTROLYTES AT ELEVATED  
TEMPERATURES (Cont)

Temperature (C)	$\Lambda$	$C \times 10^3$ (equiv/liter)
281	877	1.500
281	796	9.380
281	685	37.700
281	616	75.700
306	937	1.394
306	830	8.710
306	693	35.100
306	617	70.600

F. H<sub>3</sub>PO<sub>4</sub>

18	329.9	0.2263
18	283.2	1.9972
18	191.3	12.4825
18	122.8	49.5000
18	96.6	99.8600
25	366.1	0.2259
25	312.0	1.9942
25	208.3	12.4640
25	132.7	49.8750
25	104.1	99.7110
50	491.1	0.2239
50	401.4	1.9765
50	255.1	12.3530
50	158.5	49.4320
50	123.2	98.824
75	597.7	0.2209
75	465.9	1.9499
75	280.9	12.1870
75	170.3	48.7670
75	131.2	97.4940
100	685.1	0.2172
100	503.2	1.9174
100	288.2	11.9840
100	170.6	47.9530
100	130.6	95.8680
128	758.5	0.2121
128	517.0	1.8718
128	280.5	11.6986
128	162.3	46.8130
128	123.4	93.5890
156	801.8	0.2064
156	503.2	1.8215
156	260.0	11.3840
156	147.6	45.5560
156	111.7	91.0750

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